J. Willard Gibbs

THE
PHASE RULE
AND
PHASE REACTIONS
THEORETICAL AND PRACTICAL

BY

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PREFACE

THE march of Science leaves in its train a host of dead and dying theories, generalisations once cherished yet destined to fall victims to a remorseless scientific spirit. But a few, by reason of their very constitution, have been able to withstand the rigours of progress—the onslaught of fact after fact and idea after idea. Prominent among these we find the Phase Rule whose powers remain undimmed despite fast-gathering clouds on sub-atomic horizons. Apart from its direct utility, the application of the Phase Rule provides an excellent training in logical argument and scientific thinking, and for this reason alone it must remain a vital component of chemistry and physics curricula in schools and colleges for many years to come.

The present monograph has been written primarily for students who require a brief exposition of the principles and applications of the Phase Rule. It is intended to serve both as a theoretical and practical text-book, and covers the requirements of the Higher School Certificate and the Degree Examinations of the Universities. In view of the needs of the present-day student, whose degree of freedom is so greatly restricted by an ever-expanding syllabus, I have endeavoured to present a straightforward account of the subject while keeping in mind the type of problem the student may have to face in the examination room and in the laboratory.

The attainment of high proficiency in a subject of this nature demands a close co-ordination of theoretical studies with practical work in the laboratory, and with this in view, a number of typical experiments are described in detail. Although the student cannot be expected to perform all these experiments, I venture to suggest that the *reading of practical methods* should be encouraged as our only remedy for the mass of theory and pinch of practice which comprise the modern courses in science. The fact that a student has

no time to perform a particular experiment need not preclude him from knowing how it is done.

The adoption of simplified but comprehensive schemes of classification for the various systems has enabled me to avoid the plethora of detail which so often clouds the issue. Moreover, the diagrams have been prepared so that they may easily be reproduced by the student, and a uniform system has been preserved throughout. Thus pressure is always represented by the ordinate, concentration always by the abscissa, and temperature as abscissa or ordinate according as we are dealing with a *pt-* or *tc-* diagram. This should serve to relieve the memory tax and facilitate the correlation of the various types of systems. The pictorial summaries provide a further innovation which should prove helpful in the same connexion.

Cicero said, " There is an art in knowing a thing," but equally important for the student is the science of presenting it in a lucid and logical manner. The questions, which have been selected from actual examination papers, will furnish ample material for attaining proficiency in this direction.

It is a pleasure to record my indebtedness to Dr. H. H. Schreinemachers of Leiden, who found occasion to catalyse my interest in the Phase Rule, to Professor Kurt Fischbeck for his discourses in Bunsen's old laboratory at Heidelberg, and to Professor W. R. D. Jones of Cardiff, who has freely placed his expert knowledge of metallic systems at my disposal. I also wish to thank Messrs. R. G. Wood and T. Evans for advice on various points, and Ralph Morgan, the artist, for aid with the diagrams.

Finally, I have to express grateful acknowledgement to the various University Authorities, the School Examination Boards and the Institute of Chemistry for permission to print their copyright examination questions.

S. T. B.

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INTRODUCTORY

Look abroad thro' Nature's range,
Nature's mighty law is change.—BURNS

I. THE RANGE OF SOLID, LIQUID AND GAS

1. **The Escaping Tendency.**—All liquids tend to assume the gaseous condition and this tendency varies with the character of the liquid. Petrol, for example, evaporates at ordinary temperature more rapidly than water, and water much more rapidly than mercury, which evaporates only very slowly under these conditions.

When a liquid is in contact with a free space, molecules are continually escaping from the surface of the liquid in virtue of their kinetic energy, but at the same time molecules of the vapour are condensing, as indicated in Fig. 1. The number of molecules leaving the liquid depends on the temperature,

Vapour

Liquid

FIG. 1.
Vapour pressure

but the number of molecules recaptured by the liquid depends on the number of vapour molecules striking the surface in a given time, i.e. on the number of molecules contained in the given space and on their speed. This number and speed together determine the pressure exerted by the vapour. We see, therefore, that temperature determines the escaping tendency, or the number of molecules which escape, and pressure the capturing tendency, or the number of molecules which are captured in a given time.

When these two numbers are equal, there is equilibrium, and the temperature will correspond to a definite pressure of vapour above the liquid. This is the vapour pressure of the liquid at the temperature of the experiment. The vapour
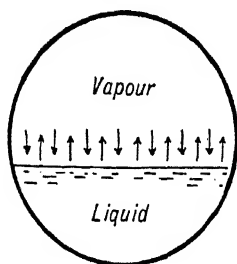
pressure of a liquid is thus the pressure of vapour with which it is in equilibrium. Vapour at this pressure is often termed " saturated vapour ", but when the pressure is less than this true equilibrium value it is designated " unsaturated vapour ".

All transformations of solid to liquid, liquid to gas and vice versa may be regarded as being due to the operation of two opposing tendencies, as indicated in the scheme—

ATTRACTIVE TENDENCY	ESCAPING TENDENCY
due to	due to
MOLECULAR ATTRACTION	THERMAL MOTION
leads to	leads to
POTENTIAL ENERGY	KINETIC ENERGY
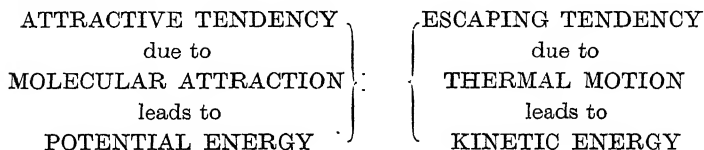
It is clear that the state of a substance depends on the balance between these two tendencies.

2. **Phases.**—A system is said to be homogeneous when it is uniform throughout its whole extent and possesses in every part identical physical properties and chemical composition.

A heterogeneous system consists of parts having different physical properties and, possibly, different chemical properties. These parts are separated from one another by bounding surfaces or interfaces. Thus, in a system consisting of ice, water and vapour, each part is in itself homogeneous and can be separated from the other parts. But the system as a whole is heterogeneous, since it contains a solid, a liquid and a gas. *The homogeneous, physically distinct parts of a heterogeneous system are called phases.* In the above system ice is the solid phase, water the liquid phase and vapour the gaseous phase. Each phase has its own characteristic vapour pressure which changes in a definite way when the temperature is raised or lowered. When equilibrium exists between the various phases the system is said to be in heterogeneous equilibrium.

3. **Coexistence of Phases.**—Since gases are miscible with one another in all proportions, two or more gases will always mix completely to form one gaseous phase. Consequently, even though a system contains a number of different gases or vapours there can be only one gaseous or vapour phase.

In the case of liquids, however, the number of coexisting phases will depend on their miscibility. Two liquids may be completely miscible, like alcohol and water, and so form one

liquid phase. Other liquids may be immiscible or only partially miscible, like ether and water, and these will form two liquid layers or two liquid phases. If to such a mixture we add mercury the system will then contain three liquid phases. It is evident, therefore, that the number of coexisting phases will depend on the miscibility relationships of the liquids under the conditions (temperature and pressure) of the experiment.

Similar remarks apply to the coexistence of solids. A heterogeneous mixture of solids consists of as many phases as there are different solid substances present. If n is the number of solids present, then the system contains n solid phases. Each individual solid and each allotropic form is a separate phase. It should be noted, however, that a solid solution or mixed crystal containing one solid actually dissolved in another solid must be regarded as a single solid phase.

4. **Equilibrium independent of Amount of Phase.**—The vapour pressure of one gram of water is exactly the same as that of one ton of water at the same temperature, and the equilibrium between water and its vapour does not depend in any way on the actual amount of water present.[1]

The same considerations apply to the equilibrium between a solid and its solution. Let us suppose that we are preparing an aqueous solution of common salt at a constant temperature $t°$. If, after shaking the mixture at this temperature, some solid salt remains at the bottom of the vessel, the solution is then saturated and its concentration is fixed. Suppose one gram of solid salt remains undissolved. If now we add a further hundred grams of salt the amount in solution will still be exactly the same, because the solution is already saturated and refuses to dissolve more. This implies that the equilibrium between the solution and the solid salt at the temperature $t°$ is independent of the amount of solid phase. To attain true equilibrium in the present case it is only necessary that *some* of the solid phase be present.

These considerations show that the equilibrium in a heterogeneous system is independent of the respective amounts of

[1] Owing to the effect of surface tension, the vapour pressure of a very small droplet is higher than the normal vapour pressure of the liquid in bulk, but the consideration of liquids and solids in such a fine state of division lies outside the purview of the ordinary Phase Rule. We are primarily concerned with macro systems and not micro systems, where the thermodynamic behaviour is influenced by surface tension.

the phases. The equilibrium is determined not by the quantity but by the quality or nature of the phases.

5. **Components.**—A component is an element or a compound which can undergo variations in concentration independently of the other constituents of the system. For the purpose of the Phase Rule the number of components is determined in accordance with the following definition :

As the components of a system we select the smallest number of independently variable constituents which are required to express the composition of each phase in the form of a chemical equation.

Or, in the words of Nernst :

The number of components in a system is the minimum number of molecular species in terms of which the composition of all the phases may be quantitatively expressed.

The essential purport of this formal phraseology will be made clear by considering some actual cases. Let us take a system consisting of ice, water and vapour. Since all three phases can be produced by physical change from water alone, there is only one component, represented by the formula H_2O. It is not correct to regard hydrogen and oxygen as two components, because the amount of hydrogen exactly determines the amount of oxygen, and vice versa. If, however, we introduce free hydrogen into the vapour phase the system becomes a two-component system, since it now contains the components H_2O and H_2.

The method of selecting the components in more complicated systems may be illustrated by reference to the case of calcium carbonate and its dissociation products. As indicated by the equation

$$CaCO_3 \qquad\qquad CaO \qquad\qquad CO_2$$

1st Solid Phase   2nd Solid Phase   Gas Phase
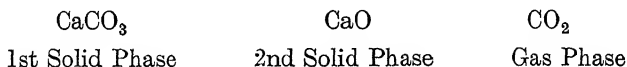
three different constituents take part in the equilibrium, but they are not to be regarded as three components, since the phases are so related that if two of them are taken, the composition of the third is defined by the equation. In fact, we can express the composition of any phase in the system in terms of any two of the constituents or molecular species. The minimum number of molecular species which must be taken

for this purpose is two, and the system is therefore a two-component system.

In the same way the composition of a salt hydrate may be expressed by an equation involving definite quantities of anhydrous salt and water. A system of the type
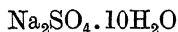
$Na_2SO_4 \cdot 10H_2O$	Na_2SO_4	$10H_2O$
1st Solid Phase	2nd Solid Phase	Liquid Phase

contains three different molecular species, but is regarded as a two-component system from the standpoint of the Phase Rule.

6. Degrees of Freedom or Variance.—*The number of degrees of freedom or variance of a system is the number of factors*
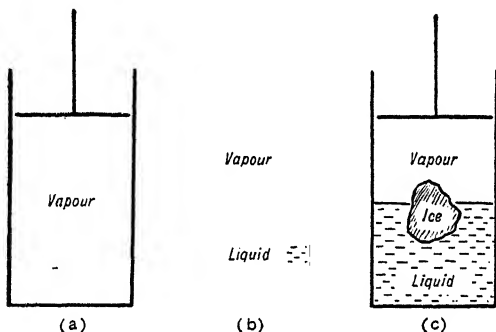
FIG. 2. Systems with different degrees of freedom

(pressure, temperature or concentration) which can be varied independently without altering the number of phases.

The precise significance to be attached to the term degree of freedom will become clear from the following considerations. Suppose we have a gas enclosed in a cylinder by means of a movable piston, as depicted in Fig. 2 (a). If we fix the volume by holding the piston in the same position, we can still vary the temperature and pressure without altering the number of phases, viz., one. Accordingly, the state of the system is undefined. Again, if we fix the temperature, we can vary the pressure and volume, and the state of the system is still undefined. But if we fix *two* of the factors, the third factor can have only one definite value. When, for example, the temperature and the pressure are fixed, the volume is also fixed, and the system is defined. Such a system in which two

factors can be varied independently without altering the number of phases is said to have two degrees of freedom.

Secondly, suppose the system (Fig. 2 (*b*)) consists of water in contact with its vapour. If now we fix one of the independently variable factors (*p* and *t*) the system will be perfectly defined. If, for instance, we fix the temperature then the pressure under which the water and vapour coexist will also be fixed. Such a system is said to possess one degree of freedom or a variance of unity.

Thirdly, let the system (Fig. 2 (*c*)) consist of ice, water and vapour in equilibrium. If we alter one of the variables the system will become unstable and the number of phases will alter. If we raise the temperature the ice will melt, while if we lower the temperature the liquid will solidify. Clearly, such a system has no degree of freedom.

7. Phase Reactions.—*A phase reaction is a physical or chemical change which involves the appearance or disappearance of a phase.* As indicated in the following scheme,
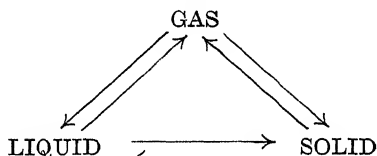
the change of solid to liquid or gas, of liquid to solid or gas, of gas to liquid or solid are phase reactions. In fact, all processes of vaporisation, sublimation, liquefaction, melting, condensation, solidification, freezing, crystallisation, precipitation, separation into two layers, allotropic change and transformation in solid solutions belong to this category.

Chemical processes may or may not be phase reactions. Thus the combination of ammonia and hydrogen chloride is a phase reaction since the two gases unite to form ammonium chloride, which appears as a solid phase :

$$\underset{\text{gas}}{NH_3} \quad + \quad \underset{\text{gas}}{HCl} \quad = \quad \underset{\text{solid}}{NH_4Cl} \quad . . . \quad \textit{phase reaction.}$$
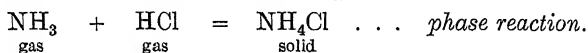
But the combination of hydrogen and chlorine is not a phase reaction because the interacting substances and the product of reaction are in the same phase :

$$\underset{\text{gas}}{H_2} \quad + \quad Cl_2 \quad = \quad 2HCl \qquad \textit{homogeneous reaction.}$$

Among phase reactions of industrial importance we may mention the preparation of salts and heavy chemicals, the Mond process for the preparation of nickel, and the many metallurgical operations involving transformations in the solid state. The science of meteorology and weather forecasting is largely concerned with phase reactions in the atmosphere, while similar changes are constantly taking place in the earth itself. On the biological side certain phase reactions, such as the evaporation of perspiration from the skin, are of vital importance to the living animal.

II. THE PHASE RULE

> But wisdom, awful wisdom ! which inspects,
> Discerns, compares, weighs, separates, infers,
> Seizes the right, and holds it to the last.—YOUNG

8. **The Rule and its Application.**—This celebrated rule was formulated in 1876 by Josiah Willard Gibbs, Professor of Mathematical Physics at Yale University. Published in an obscure journal[1] and developed in somewhat rigorous mathematical fashion,[2] its essential value to the chemist was not immediately recognised. Gibbs, it seems, was fully aware of the importance of his work, but he could hardly have realised how greatly it was to influence the subsequent developments of chemistry, metallurgy and geology.

The Phase Rule may be expressed in the simple form

$$P + F = C + 2,$$

where P = number of phases, F = number of degrees of freedom and C = number of components in a system in equilibrium. The mass of the phase does not enter into the equation, since of course it has no influence on the state of equilibrium.

As a preliminary indication of the manner in which the Phase Rule is applied we may cite the following cases.

(a) *Bivariant Systems.*—Consider a one-component system

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[1] *Trans. Conn. Acad.*, 1876, **3**, 152 ; *Scientific Papers*, **1**, pp. 62-100.

[2] During his long academic career Willard Gibbs is reputed to have made only one public speech, one of the shortest on record : " Mathematics is a language ".

consisting entirely of vapour. Applying the Phase Rule, we have

$$1 + F = 1 + 2,$$
$$F = 2.$$

This agrees with the fact previously indicated (p. 5) that if the system consists of one phase, both the temperature and the pressure can be varied independently. Systems which can undergo two independent variations without change in the number of phases have two degrees of freedom and are termed *bivariant systems*.

(b) *Univariant Systems.*—If we have a one-component system consisting of liquid and vapour, then P = 2, C = 1,
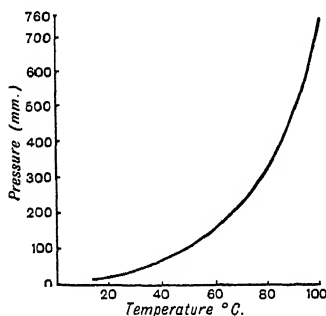
Fig. 3. Vapour pressure of Water
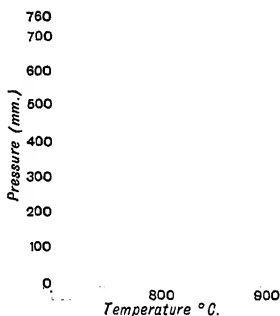
Fig. 4. Dissociation pressure of Calcium Carbonate

and we find from the Phase Rule that F = 1. Such a system can undergo only one independent variation in the factors (*p, t, c*) without alteration in the number of phases and is said to be *univariant*.

We may consider in this connexion the dissociation of calcium carbonate as represented by the equilibrium

$$CaCO_3 \; \underset{\longleftarrow}{\overset{\longrightarrow}{}} \; CaO \quad + \quad CO_2.$$

Since P = 3 and C = 2, the Phase Rule gives F = 1, so that the system is univariant. This system is outwardly quite different from the above water/vapour system,[3] but the Phase Rule

[3] The equilibrium between a phase A and a phase B may be expressed symbolically by A|B. Apart from its suggestion of equilibrium at an interface or along a curve, it serves to avoid confusion with the overworked representation A–B, which may signify a two-component system or a compound between A and B.

postulates that they should behave in a similar manner since both systems are univariant. This is borne out by experiment, as may be seen from the curves in Fig. 3 and Fig. 4. To each temperature there corresponds a definite pressure, and the dissociation pressure curve of calcium carbonate is essentially similar to the vapour pressure curve of water.

(c) *Invariant Systems.*—For a one-component system consisting of ice, water and vapour we have P = 3, C = 1, and from the Phase Rule F = 0. Such a system cannot undergo the slightest variation in any of the factors (*p, t, c*) without suffering an alteration in the number of phases, and is said to be *invariant.*

9. **Advantages of the Phase Rule.**—The Phase Rule is one of the most beautiful and comprehensive generalisations known to the chemist. Essentially, it provides us with a simple method of classifying states of equilibrium. Systems having the same number of degrees of freedom behave in like manner under the influence of variations in temperature, pressure and volume (or concentration).

Any change which involves the appearance or disappearance of a phase is a phase reaction, and it is here that the Phase Rule proves a veritable " master-key " for unlocking the mysteries and elucidating the frequently complex phenomena which occur in physico-chemical systems. In this connexion it offers the following advantages :

(*a*) widely different physical and chemical systems may be classified and their behaviour predicted ;

(*b*) it is not necessary to take into account the molecular complexity of the substances ;

(*c*) it is not necessary to make any assumptions with regard to the constitution of matter.

The Phase Rule takes no cognisance of the nature or the amounts of the substances, nor of the nature of the phase reactions, whether they be chemical or physical, nor of the time taken for the transformation or change of state. Actually, the rule itself merely tells us how many phases will be present in a system, but applied in conjunction with experiment we are invariably able to specify what these phases will be.

It is here that the Phase Rule scores over the Law of Mass Action, which cannot tell us whether a number of given substances will or will not remain in equilibrium or whether

equilibrium is possible after some of them have been transformed into new substances.

10. **Limitations of the Phase Rule.**—In using the Phase Rule as expressed in the above equation, the following limitations must be borne in mind :

(a) all phases in the system must be under the same pressure and gravitational force ;

(b) no liquid or solid phase shall be so finely divided that the vapour pressure or fugacity is affected by surface tension ;

(c) the only variables which shall be allowed to affect the system are temperature, pressure and composition ; electric, magnetic and actinic influences are thus excluded.

In a few special cases, where additional restrictions must be made in applying the Phase Rule, the effect of each restriction is to reduce the number of degrees of freedom by one. For example, the system comprising ammonium chloride in equilibrium with its dissociation products

$$NH_4Cl \qquad NH_3 \quad + \quad HCl$$

is a one-component system, since the restriction is imposed that the NH_3 and HCl shall always be in the molecular proportion $1 : 1$. By the Phase Rule this one-component system will have $F = 1$. If, however, we add excess of NH_3 (or of HCl) the system becomes a two-component system, and now $F = 2$. Clearly, therefore, the restriction that the ratio of NH_3 to HCl is to be exactly $1 : 1$, or that the composition of the gaseous phase is to be the same as that of the solid phase, reduces the number of degrees of freedom by one.

The effect of such restrictions must also be taken into account in dealing with critical phenomena. At the critical point there is the additional restriction that the two phases shall be identical, and this reduces the number of degrees of freedom of the system by one. Similar considerations apply to the critical solution temperature of two liquids. Apart from these special cases, which are dealt with later, the application of the Phase Rule is invariably simple and straightforward.

11. **" New Phase—New Curve."**—If two phases happen to have identical vapour pressure equations they are thermodynamically identical and as such will be classed as one phase

from the standpoint of the Phase Rule. Thus two crystals of the same molecular species which differ merely in the fact that one is the mirror image of the other are generally considered as one and the same phase. But each polymorphic form and each allotropic modification constitutes a separate phase, since these forms are associated with different amounts of energy and have different vapour pressure equations.

In so far as the " topography " of phase diagrams is concerned, the rule " New Phase—New Curve " is the basis of the code which we must observe along the highways and the cross-roads of the thermodynamic domain. Each phase has its own curve of equilibrium and the occurrence of a phase reaction is always signalled by the intersection of two curves.

12. **The Question of Isotopes.**—With the exception of hydrogen and deuterium compounds, which have different physical and chemical properties, isotopes and the corresponding isomolecules are generally regarded as one molecular species since they behave in the same way towards pressure and temperature changes. Mercury, for example, is known to contain nine isotopes, but, owing to the practical identity of their vapour pressure equations, the element is considered to be a one-component system for our present purposes. Similar remarks apply to systems containing isomolecules, such as HCl^{35} and HCl^{37}.

If, however, an element, free or combined, is converted into one of different atomic number as a result of spontaneous nuclear transformation or atomic bombardment, the new substance must be regarded as an additional component.

13. **Deduction of the Phase Rule.**—The following outline will serve to illustrate the essential argument employed in the derivation of the Phase Rule :

Let the system attain equilibrium.

Let P = number of phases and C = number of components.

Before we can fix the composition of a phase we must know $(C-1)$ composition-variables.

In order to fix the composition of P phases, therefore, we must know $P(C-1)$ composition-variables.

In addition, there are the two variables, temperature and pressure, so that

$$\text{Total Number of Variables} = \underset{\text{(concns)}}{P(C-1)} + \underset{\text{(temp.)}}{1} + \underset{\text{(press.)}}{1}$$
$$= P(C-1) + 2.$$

For each phase there will be an equation of state connecting its variables.   For each component there will be $(P-1)$ equations, so that

Total Number of Equations for C components $= C(P-1)$.

Let $F =$ difference between the number of variables and the number of equations connecting them, i.e. the number of degrees of freedom of the system.

Accordingly, we have

$$F = [P(C-1)+2] - [C(P-1)]$$
$$= C + 2 - P$$
$$\text{or } P + F = C + 2.$$

ONE-COMPONENT SYSTEMS

14. Method of Representation.—The condition of a system of one component (i.e. a pure substance) is completely determined by two variables only, the temperature and the pressure. The behaviour of the various phases in such a system can be represented graphically by means of a pressure-temperature diagram. A complete representation of this kind gives a pictorial indication of the phase reactions and the nature of the equilibria between the various phases, and for this reason it is commonly called an *equilibrium diagram*.

With a view to illustrating the principles involved in the construction and interpretation of equilibrium diagrams we shall consider in some detail the behaviour of the various phases of water.

I. WATER

> Unto the place from whence the rivers come,
> thither they return again.—Ecclesiastes i. 7

15. The Vapour Pressure Curve of Liquid Water.—The vapour pressure of every liquid increases with rise of temperature. If we plot the vapour pressure of water against the temperature we obtain the vapour pressure curve, represented by the line OAK in Fig. 5.[1]

It shows that the vapour pressure of the liquid increases as the temperature is raised. At A, the normal boiling point, 100°, the vapour pressure becomes equal to one atmosphere or 760 mm. Hg. When a liquid boils, heat must be supplied in

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[1] The equilibrium diagrams, which we employ for purposes of discussion, are not always drawn to scale and are frequently exaggerated in order to give prominence to the character of the essential relationships.

order to convert it into vapour. Since the boiling point is
constant, the heat supplied does not produce a rise of tem-
perature but is entirely used up in converting the liquid into
vapour. This quantity of heat, which may be regarded as
hidden or latent in the vapour, is termed the latent heat of
vaporisation. When, for example, 1 gram of water at 100°
is changed into vapour or steam at 100°, 538 calories of heat
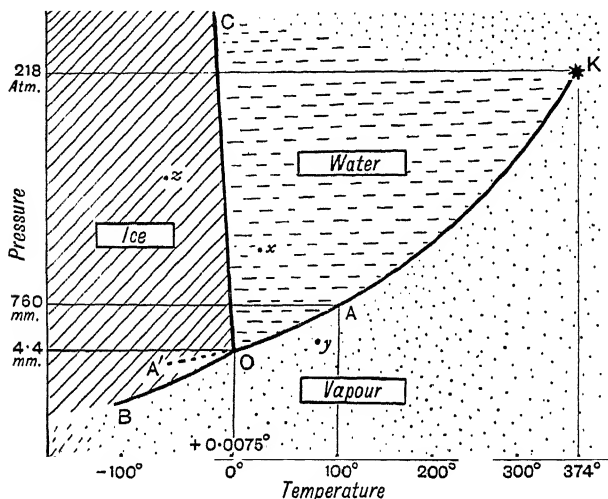
FIG. 5.   Equilibrium diagram of Water

are absorbed; similarly, when 1 gram of vapour at 100°
condenses to liquid at 100°, 538 calories are evolved.

The effect of heating or cooling a system in equilibrium
may be predicted by the application of the *Le Chatelier
principle*, or, as it sometimes is called, the *Principle of Mobile
Equilibrium*. The principle may be stated as follows : *If a
constraint is imposed on a system in equilibrium, the equilibrium
will shift in such a way as to relieve the effect of the constraint.*
This principle is universal, for it applies to all physical and all
chemical systems in equilibrium. If we apply heat to a
liquid/vapour system, the equilibrium will change in such a
way that heat is absorbed. Since vaporisation is accompanied
by the absorption of heat, it follows that liquid will be con-
verted into vapour and the pressure in the system increased.

The Le Chatelier principle predicts that the vapour pressure of a liquid will always increase with rise of temperature, because vaporisation is always accompanied by the absorption of heat.

The qualitative effects predicted by the Le Chatelier principle can be expressed quantitatively by means of the Clapeyron equation, which may be written

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{l}{T(v_2 - v_1)},$$

where $\mathrm{d}p$ is the increment of pressure, $\mathrm{d}T$ the increment of temperature, l latent heat of vaporisation per gram, v_2 the specific volume of the vapour,[1] v_1 the specific volume of the liquid and T the absolute temperature at which the change takes place. The equation shows that the rate of change of vapour pressure with temperature depends on the latent heat, and if we know the one we can calculate the other.

Since the specific volume of the vapour is so much greater than that of the liquid, we can neglect v_1. If we refer the quantities to 1 gram mole of the substance we have

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{TV},$$

where L is the latent heat of vaporisation of 1 gram mole and V is the volume of 1 gram mole of the vapour. Assuming now that the gas laws hold for the vapour, we may write

$$V \qquad p \quad ,$$

which, substituted in the above equation, gives

$$\frac{1}{p} \cdot \frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{RT^2}.$$

But we know from the " differential calculus " that

$$\frac{1}{p} \cdot \frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\mathrm{d} \log_e p}{\mathrm{d}T},$$

and hence

$$\frac{\mathrm{d} \log_e p}{\mathrm{d}T} = \frac{L}{RT^2}.$$

If, further, we assume that the latent heat does not vary appreciably over the temperature interval T_1 to T_2, we can integrate this equation and obtain

$$\log_e \frac{p_2}{p_1} = \frac{L(T_2 - T_1)}{RT_1 T_2}.$$

[1] The specific volume is the volume of 1 gram of the material.

Since $R = 2$ cal. (approx.) and $\log_e x = 2 \cdot 303 \log_{10} x$, we have

$$\log_{10} p_2 - \log_{10} p_1 = \frac{L(T_2 - T_1)}{2 \cdot 303 \times 2 \times T_1 T_2},$$

where p_1 and p_2 are the vapour pressures at the temperatures T_1 and T_2. This equation may be used to calculate the vapour pressure values if we know the vapour pressure at a given temperature. Alternatively, it may be employed to calculate the latent heat from known values of the vapour pressure.

16. **The Vapour Pressure Curve of Ice.**—Ice, like water, has a vapour pressure or sublimation curve of its own. The vapour pressure, though small, is real, and may be measured quite easily in a suitable tensimeter.[1] The vapour pressure of ice also increases with rise of temperature, as indicated by the curve BO. This curve is not a continuation of OA, but is a separate and distinct curve in conformity with the rule " New Phase—New Curve ". The water curve and the ice curve intersect at O, and this intersection implies that, at the temperature corresponding to the point O, ice and water have the same vapour pressure, i.e. they are in equilibrium.

Water at its freezing point is in equilibrium with ice and it is at this point alone that ice and water can coexist in any proportions whatever. Normally, we have to deal with water and ice coexisting under a pressure of one atmosphere, and the temperature of coexistence under these conditions is exactly $0°$ C. But let us do away with this external pressure and allow the ice and water to coexist simply under the pressure of their own vapour, as, for example, in an evacuated flask. The vapour pressure under these conditions is $4 \cdot 6$ mm., and experiment shows that when the pressure is thus reduced from 760 mm. to $4 \cdot 6$ mm. the freezing point is raised from $0°$ to $+0 \cdot 007°$ C. It follows, therefore, that the point O represents a temperature $0 \cdot 007°$ higher than the freezing point under ordinary atmospheric pressure.

At any point on the curve OAK water and vapour coexist in equilibrium ; at any point on the curve OB ice and vapour are in equilibrium. At the point O, where the two curves

[1] Advantage is taken of the vapour pressure of solids in the widespread use of solid perfumes and cosmetics. The use of naphthalene and p-dichlorobenzene in " moth-balls " also depends on the fact that these substances have a sensible vapour pressure at ordinary temperature, and produce a concentration of vapour too " high " for the olfactory comfort of the moth.

intersect, the three phases, ice, water and vapour, can exist together in equilibrium. Such a point is called a *triple point*, and here solid and liquid are in equilibrium under a pressure equal to their vapour pressure.

17. **The Freezing Point Curve.**—The normal melting point or freezing point of a pure substance is defined as the temperature at which the solid and the liquid are in equilibrium under a pressure of one atmosphere. The application of external pressure to a freezing liquid will necessarily alter the freezing point. In the case of water the effect of pressure is shown by the curve *OC*, drawn from the triple point. This curve gives the temperatures at which ice and water are in equilibrium under various pressures. Since the melting point of ice is lowered by the application of pressure, the curve slopes towards the left, but only slightly, because the effect of pressure is small.

The effect of pressure on the melting point of a solid may be predicted by means of Le Chatelier's principle (p. 14). When we increase the pressure on a solid and liquid in equilibrium at the melting point, the phase with the larger specific volume will tend to disappear. If the solid has the greater specific volume some of it will melt, latent heat of fusion will be absorbed and the temperature at which equilibrium is reestablished, i.e. the new melting point, will be lower. This is the behaviour exhibited by ice and a few other substances, such as bismuth and the type metals, which expand on freezing. On the other hand, if the liquid has the greater specific volume, pressure will cause some of the liquid to solidify, latent heat of solidification will be evolved, and the new equilibrium temperature or melting point will be higher. Sulphur, benzene and most other substances behave in this way and contract on freezing.

The Clapeyron equation may be used to calculate the effect of mechanical pressure on the melting point of any substance. The equation may be written in the form

$$\mathrm{d}T = \frac{\mathrm{d}p(v_2 - v_1)\,T}{l},$$

where $\mathrm{d}T$ is the change in melting point, $\mathrm{d}p$ the pressure increment, v_2 the specific volume of the liquid, v_1 the specific volume of the solid, T the melting point on the absolute scale and l the latent heat of fusion per gram.

We may calculate the effect of pressure on the melting point of ice in the following way. At 0° C. or 273° T, 1 gram of water occupies 1·000 c.c. but 1 gram of ice occupies 1·091 c.c. The latent heat of fusion is 80·04 cal. per gram, which is equal to $80·04 \times 4·2 \times 10^7$ ergs, since the mechanical equivalent of heat is $4·2 \times 10^7$.

The pressure increment corresponding to 1 atmosphere expressed in dynes per sq. cm. is given by

$$dp = 76·0 \times 13·6 \times 981 = 1·013 \times 10^6 \text{ dynes per sq. cm.,}$$

since the density of mercury is 13·6 and g is 981 cm./sec.².

Substituting in the Clapeyron equation we have

$$dT = \frac{1·013 \times 10^6 \times (-0·091) \times 273}{80·04 \times 4·2 \times 10^7} = 0·0075°.$$

The melting point of ice will thus be lowered by 0·0075° for each additional atmosphere of pressure applied to it. Actually, Lord Kelvin found that the melting point was depressed by 0·0072° per atmosphere increase. The above calculation also shows that the triple point is 0·0075° higher than the normal freezing point under atmospheric pressure.[1]

18. **The Equilibrium Diagram.**—An equilibrium diagram of similar type to that shown in Fig. 5 can be constructed for any pure (one-component) substance. Such a diagram consists of a number of regions (or areas), lines and points of intersection. The significance of these characteristic features of the diagram may now be discussed in turn.

(a) *Regions.*—The diagram consists of three regions, which may be labelled " solid ", " liquid " and " vapour " respectively. Suppose we have a mass of water in the state represented by the point x and that we now alter the pressure and the temperature to correspond to the values at the point

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[1] It is commonly believed that the movement of glaciers is due in part to the melting produced by pressure. It has also been suggested that ice-skating is made possible by the incipient melting of the ice under the skate. Recently, however, it has been demonstrated that it is just as easy to skate on borax, which cannot melt under such conditions.

Faraday noticed that two pieces of thawing ice when pressed together froze into one continuous mass at the surface of contact. This process of re-freezing, misguidedly termed *regelation,* should not be confused with the pressure effects discussed above. Since the film of water between the two pieces of ice is isolated from external heat radiations, it freezes and binds the pieces together. It is in virtue of this phenomenon that it is possible to make a snowball.

y. We should find that the water is completely converted into vapour during this operation. Similarly, if we bring the water to the temperature and pressure corresponding to the point z, it will be converted entirely into ice. For the different regions we have

p and t corresponding to points in area BOC—solid ⎫
p and t corresponding to points in area AOC—liquid ⎬ One
p and t corresponding to points in area BOA—vapour ⎭ phase.

Applying the Phase Rule $P + F = C + 2$

Number of phases $= 1$; Number of Components $= 1$.

Substituting, we have $1 + F = 1 + 2$,
whence $F = 2$.

Since the system has two degrees of freedom, it is bivariant, and the two factors, pressure and temperature, can be varied independently without altering the number of phases, viz. one.

(b) *Boundary Lines.*—On the curves or boundary lines two phases can coexist in equilibrium :

At points on the curve OAK—water/vapour ⎫
At points on the curve OB—ice/vapour   ⎬ Two
At points on the curve OC—ice/water   ⎭ phases.

The curve OAK shows that for each temperature there is only one pressure of vapour with which the liquid is in equilibrium. If, at constant temperature, we attempt to increase the pressure on such a system all the vapour will condense to liquid. On the other hand, if we slightly decrease the pressure, all the liquid will evaporate or boil away to vapour. Clearly, then, for each temperature there is only one value—a fixed value—for the pressure.

In the same way, the curve OB indicates that for each temperature there can be only one, fixed pressure at which solid and vapour coexist in equilibrium. Similarly, the curve OC shows that for each temperature the pressure at which liquid and solid coexist in equilibrium can have one value only.

Applying the Phase Rule to the system when it consists of two phases, we have
$$2 + F = 1 + 2$$
and $F = 1$.

Such a system is univariant, and the pressure and temperature

cannot be varied independently without altering the number of phases.

(c) *The Triple Point.*—At the triple point O all three phases—solid/liquid/vapour—are in equilibrium. Applying the Phase Rule, we have

$$3 + F = 1 + 2$$

and $$F = 0.$$

Since the system has no degree of freedom it is invariant. This implies that we cannot alter the pressure or the temperature without altering the number of phases. If, at constant pressure, we raise the temperature, the ice and water will be converted into vapour. On the other hand, if we attempt to lower the temperature, vapour will be deposited as ice and the water will freeze. The triple point possesses, therefore, rigidly fixed, unalterable values for the temperature and the pressure.

19. The Critical State.—The curve OA separates the region of vapour from the region of liquid, but the separation is not complete under all conditions. As we have seen, this curve represents the vapour pressure of the liquid, but there is a limiting value beyond which the vapour pressure of a liquid cannot rise. This is the *critical pressure*, and it is attained at the *critical temperature*. There is, therefore, an abrupt termination to the curve OA at the *critical point K*. Above this point, liquid and vapour are indistinguishable, for the two phases have become identical. When we apply the Phase Rule to the system at this particular point, we must subtract one degree of freedom because of the extra restriction that the two phases are to be identical (p. 10). For the system at the critical point we have

$$2 + F = 1 + 2 - \text{Identity Restriction}$$

so that $$F = 0.$$

The critical point is thus an invariant point with fixed values for the temperature and the pressure.

No liquid can exist above the critical temperature and it is always necessary to cool a gas below this point before liquefaction can occur under applied pressure.[1]

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[1] With regard to the terminations of the other curves, it is obvious that the solid/vapour curve OB must end at zero pressure and absolute zero temperature. Matters are not quite so obvious in the case of the solid/liquid curve OC. Where does it end ? Is there also a solid/liquid

20. **The Metastable State.**—In the foregoing discussion we have confined our attention to the stable states of water. However, as Fahrenheit observed in 1724, it is possible to cool water below its freezing point, so that it is in a metastable condition. It may, therefore, exist as liquid below the freezing point, and in this condition, it is said to be *supercooled*. Such supercooled water also has a vapour pressure, which changes in normal fashion with temperature. The vapour pressure curve of supercooled water is indicated by the dotted continuation of the curve *AO*. This curve, *OA'*, lies above the vapour pressure curve of ice, and it is evident that the vapour pressure of the supercooled liquid is greater than that of the solid. This statement may be embodied in the form of a general rule : *The vapour pressure of the metastable phase is always greater than that of the stable phase.* As will be shown later, this rule is of great utility in enabling us to decide whether we are dealing with a metastable or stable phase.[1]

II. THE DIFFERENT FORMS OF ICE

21. **The Effect of High Pressure on Ice.**—The researches of Tammann and of Bridgman have shown that water can exist in at least seven different crystalline forms, all of which, with the exception of ordinary ice, are denser than water. These polymorphic forms of ice are known as Ice I, Ice II, Ice III, Ice IV (unstable), Ice V, Ice VI and Ice VII.

The polymorphic forms are produced at high pressures, and differ from the ordinary variety (Ice I) in density, crystal

critical point analogous to the liquid/vapour critical point ? No one knows, but the student will recognise that there is a fundamental difference between the two cases. In the liquid and vapour phases there is random arrangement and haphazard movement of the molecules, so that a continuous passage from one to the other is possible. But in the solid the molecules (or ions) are marshalled in a definite space lattice as a result of the operation of interatomic and intermolecular forces.

[1] Metastable equilibrium is a state in which the system preserves a pseudo stability. Such a system may become unstable through certain disturbances and thus change into a state of stable equilibrium. A spoon balanced on the edge of a tea-cup is in metastable equilibrium ; it may last for a long time in this position, but if suitably disturbed it will fall into the cup and thus assume stable equilibrium. This is an example of mechanical equilibrium, and its analogy with physico-chemical equilibrium, like all analogies, must not be pushed too far.

structure, heat of formation and other physical properties. The range of existence of the various modifications is shown in Fig. 6.

With the exception of the unstable Ice IV, each variety of ice has definite pressure and temperature limits within which
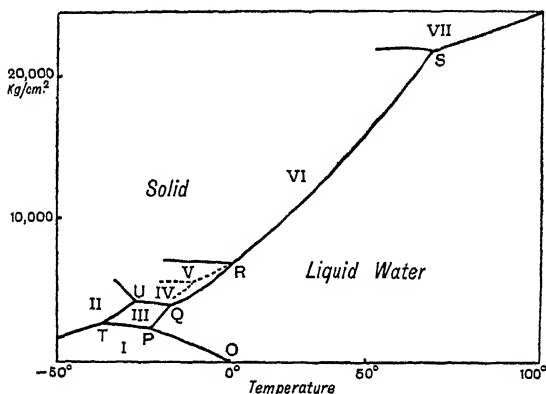
FIG. 6.   The seven polymorphic forms of Ice

it is perfectly stable. The boundary curves represent univariant systems, while the points are triple points at which three phases coexist at the invariant temperature and pressure. As may be seen from the following table, these triple points lie in regions where the vapour phase cannot exist.

THE POLYMORPHIC FORMS OF ICE

Triple Point	Temperature	Pressure	Phases
O	$+ 0.0075°$	4·6 mm. Hg	Ice I/liquid/vapour
P	$-22°$	2,115 kg.-cm.^{2}	Ice I/Ice III/liquid
Q	$-17°$	3,530 ,,	Ice III/Ice V/liquid
R	$+ 0.16°$	6,380 ,,	Ice V/Ice VI/liquid
S	$+81.6°$	22,400 ,,	Ice VI/Ice VII/liquid
T	$-34.7°$	2,170 ,,	Ice I/Ice II/Ice III
U	$-24.3°$	3,510 ,,	Ice II/Ice III/Ice V

Incidentally, it will be noted that both Ice VI and Ice VII are stable above 0°. In fact, Ice VII is solid at the normal boiling point of water (100°) and the melting point curve has

actually been carried up to 190° under a pressure of 40,000 kg.-cm.².

III. DEUTERIUM OXIDE

22. The Phases of Deuterium Oxide.—Deuterium oxide, or heavy water, occurs in ordinary water to the extent of 1 part in 4000, and may be isolated therefrom by fractional electrolysis. Although hydrogen and deuterium are isotopes the corresponding oxides differ markedly in physical properties, as may be seen from the following table :

Property	Protium Oxide H_2O	Deuterium Oxide D_2O
Molecular Weight . . .	18	20
Density 25°/25° . . .	1·000	1·1079
Maximum Density Temperature	4·0°	11·6°
Freezing Point . . .	0·00°	3·82°
Heat of Fusion . . .	1,436	1,510 cal.
Mol. Volume of Ice . . .	19·65	19·32 c.c.
Boiling Point	100·00°	101·42°
Heat of Vaporisation . .	10,484	10,743 cal.

The equilibrium diagram for heavy water (Fig. 7) is similar to the diagram for ordinary water (Fig. 5), but the triple point O is 3·82° higher, while the vapour pressure of the liquid becomes equal to 760 mm. at 101·42°. Heavy water expands on freezing and the melting point is lowered by 0·0069° for each atmosphere of pressure applied. The freezing point curve OC therefore slopes to the left but to a slightly lesser extent than the corresponding curve for water.

The fact that the melting point of D_2O is higher than that of H_2O can be explained on the basis of the Wave Mechanical Theory of the Atom. The

FIG. 7. Deuterium Oxide

energy which a molecule possesses at absolute zero is called the *zero-point energy*. It betrays itself in the atomic vibrations
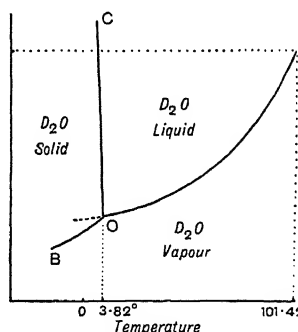
within the molecule, which never cease even at the point of " heat-death " (−273°). This energy is inversely proportional to the atomic mass, and since the mass of D is twice that of H, the zero-point energy of D_2O will be lower than that of H_2O. This implies that more external energy must be given to a molecule in solid D_2O in order to shake it free into the liquid phase. In other words, a higher temperature is necessary to melt solid D_2O than solid H_2O.

There are six polymorphic forms of solid deuterium oxide (heavy ice) : D_2O I (m.p. 3·82°), D_2O II, D_2O III, D_2O IV (unstable), D_2O V and D_2O VI. The equilibrium diagram[1] is similar to the diagram for ordinary ice (Fig. 6), but the triple points occur at higher temperatures.

IV. CARBON DIOXIDE

But during this period of commercial obscurity one cannot say that solid CO_2 was born to sublime unseen, for experimenters turned to it thankfully as a means of obtaining low temperatures, and lecturers found it invaluable for teaching students of the Phase Rule the grand basic truth that substances can, and some substances do, have their boiling points colder than their freezing points.—H. G. LITTLER

23. **Liquid Carbon Dioxide.**—Faraday liquefied carbon dioxide in 1823 by subjecting the gas to the simultaneous action of pressure and cold in his well-known sealed tube arrangement. Today, the liquid is prepared in large quantities by forcing the gas into steel cylinders by compression pumps ; at ordinary temperature the gas is converted into liquid under a pressure of about 50 atmospheres.

Liquid carbon dioxide is a colourless mobile liquid boiling at −78° under ordinary atmospheric pressure. When the liquid is allowed to escape from the cylinder into the air, it absorbs so much heat during the rapid evaporation that some of it is frozen into snow-like solid carbon dioxide (p. 239).

24. **The Equilibrium Diagram.**—In Fig. 8 *BO* is the vapour pressure or sublimation curve of solid carbon dioxide and *OA* the vapour pressure curve of the liquid, while *OC* represents the effect of pressure on the melting point of the solid. The uniqueness of this system arises from the fact that

[1] Bridgman, *J. Chem. Physics*, 1935, 3, 602.

the triple point O lies above atmospheric pressure. Owing to this circumstance it follows that (a) the solid, liquid and gas cannot exist together at atmospheric pressure and (b) solid
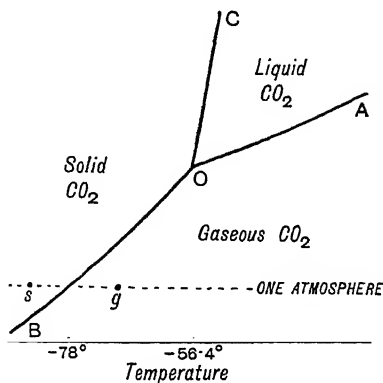
Fig. 8.   Equilibrium diagram of Carbon Dioxide

carbon dioxide under ordinary pressure, as at s, will pass directly into gas, as at g, without the intermediate formation of liquid.   It is partly in virtue of these properties that solid carbon dioxide finds so many applications.

If we apply the Phase Rule to the system solid CO_2/gaseous CO_2 we have

$$2 + \mathrm{F} = 1 + 2,$$

Since the system is univariant it follows that if we change the pressure of the gas above the solid the temperature of the solid material will alter.   In fact, this is known to happen when commercial blocks of the solid are removed from their containers.

25. **Solid Carbon Dioxide.**—Although Thilorier succeeded in solidifying carbon dioxide in 1835 it was not manufactured commercially until 1924, when suitable plant was erected in Montreal.[1]

The liquid carbon dioxide is throttled to one atmosphere

[1] The first patent was taken out some thirty years previously by Elworthy, a British Army doctor stationed in India.   He conceived the idea of using the gas from solid carbon dioxide for preparing good whisky and soda while on the march.

and the carbon dioxide " snow " thus formed is compressed
hydraulically into blocks of " dry ice ". In this way 30 per
cent of the liquid is converted into solid and 70 per cent into
gas, which is collected and reliquefied.

Since the ordinary temperature is so much higher than the
temperature of " dry ice " it would be reasonable to suppose
that the solid would evaporate away extremely rapidly.
Actually, however, this is far from being the case, because the
solid has a high latent heat (87·2 cal. per gram) and a high
density (1·56), and because, moreover, it surrounds itself with
an insulating blanket of heavy vapour. It may, therefore,
be stored for long periods and sent over long distances in
suitable containers without serious evaporation losses.

Advantages and Uses.—In comparison with ordinary ice
solid carbon dioxide has the following advantages as a re-
frigerant :

    (*a*) it is able to produce a lower temperature (− 78°) ;
    (*b*) it passes directly into vapour, leaving no liquid to be
        collected or led away ;
    (*c*) it occupies less space ;
    (*d*) it has a higher latent heat and a greater density so
        that the over-all cooling effect is about twice as
        efficient as that of ordinary ice ;
    (*e*) it forms excellent freezing mixtures with many organic
        liquids ;
    (*f*) the evolved gas has a marked germicidal effect in many
        cases.

Among the many uses of solid carbon dioxide we may
note the following :

(1) Storage and transport of ice-cream, e.g. in ice-cream
tricycles.

(2) Preservation of foodstuffs in refrigerators. The bacteri-
cidal effect of carbon dioxide enables fish to be transported
over long distances.

(3) Aeration with carbon dioxide in the mineral water
industry.

(4) Shrinkage-fitting of machine parts. In fitting a bush
into a bearing, for example, the bush is first immersed in an
oil-bath cooled with " dry ice " and then inserted into the
bearing. In this way a tight fit is obtained when the metal
regains ordinary temperature.

(5) Thermal cauterisation. Cauterisation by means of solid carbon dioxide has been used in hospitals for many years. In this way the temperature of the affected part of the body may be reduced by over a hundred degrees.

Curiously enough, solid carbon dioxide is not suitable for making ice-cream because the frozen particles are too coarse for the palate, but as stated above it is widely used for preserving ice-cream which has been prepared by the ordinary methods of freezing.

V. SULPHUR

See plastic Nature working to this end
The single atoms each to other tend,
Attract, attracted to, the next in place
Formed and impelled its neighbour to embrace.—POPE

26. **Transition Phenomena.**—The ordinary form of sulphur is the rhombic variety and this exhibits a curious behaviour on heating. When heated rapidly, it melts at 115°, but when heated slowly it changes into the monoclinic form which ultimately melts at 120°. When the monoclinic variety is cooled it passes slowly into the rhombic modification as indicated in the scheme

$$\text{Rhombic Sulphur} \underset{\longleftarrow}{\overset{95\cdot5°}{\longrightarrow}} \text{Monoclinic Sulphur}$$
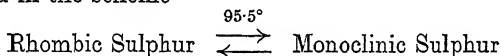
The transformation or phase reaction takes place at 95·5°, and this temperature is called the *transition point* or *transition temperature*. Below the transition point rhombic sulphur is stable, above it metastable. Above the transition point monoclinic sulphur is stable, below it metastable. At the transition point both forms are equally stable and can exist side by side in stable equilibrium.

A transition point of this kind is comparable in some respects with a melting point. At the melting point latent heat of fusion is absorbed and there is equilibrium between the solid and liquid phases ; at the transition point, however, latent heat of transformation is absorbed and there is equilibrium between two solid phases. The chief difference lies in the fact that a crystalline solid can never be heated above its melting point without actually fusing, whereas a substance like rhombic sulphur can be heated above the transition

temperature without undergoing sensible change. The essential distinction between the two cases may be represented as follows :

MELTING POINT

Solid I $\rightleftarrows$ Liquid
(Space lattice I)   (No space lattice)

TRANSITION POINT

Solid I $\vdots$ Solid II
(Space lattice I)   (Space lattice II)
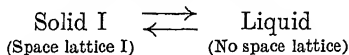
The atoms or molecules in a crystal are arranged in a characteristic three-dimensional lattice [1] and are in continuous vibration about certain mean positions in virtue of thermal energy. When the crystal is heated the amplitude of vibration increases until the melting point is reached, when the thermal tolerance is exceeded and a complete break-down of space lattice occurs. On the other hand, a transition process merely involves a change into another space lattice, characteristic of the second modification. The transition is effected through small translatory, and possibly rotatory, movements of the atoms or molecules in the lattice. Intermolecular forces are strongly operative in a solid and serve to prevent immediate adjustment of the system to the new thermal conditions imposed upon it. It is in virtue of this *hysteresis* or molecular lag that it is possible to heat rhombic sulphur above the transition point without appreciable change into the monoclinic form. If the change is to be effected, the system must be heated to the transition point and given sufficient time for adjustment to the new thermal conditions.

The X-ray analysis of rhombic sulphur shows that it contains the S_8 molecule, which is a symmetrical puckered ring with S—S distance 2·12 Angstroms,[2] and bond angle 105° :
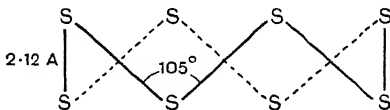
The configuration of the molecule as seen parallel to and perpendicular to the axis of the ring is shown in Fig. 9. The

[1] A *space lattice* is an arrangement of rows of points in space such that the environment of any point is the same as that of every other point.   [2] 1 Angstrom A $= 10^{-8}$ cm.

actual crystal is built up by the neat packing of the molecules against one another. The spatial characteristics of monoclinic sulphur have not been determined up to the present, but it is believed that the molecule is also S_8 in this modification and in the melt at temperatures immediately above the melting point.[1]

27. **The Equilibrium Diagram.**—The various equilibria which may occur in the case of the element sulphur may be represented by a pt-diagram as shown in Fig. 10. The line RO is the vapour pressure curve of rhombic sulphur; it shows the change in the vapour pressure of this modification with temperature. Similarly, OM is the vapour pressure curve of monoclinic sulphur; it represents the change in vapour pressure of monoclinic sulphur with temperature. The two curves intersect at the transition point O, where the two modifications have the same vapour pressure and are therefore equally stable.

Below the transition temperature the vapour pressure of the metastable phase is greater than that of the stable phase, in accordance with the metastability rule (p. 21). The curve OM', which lies above the curve OR, represents the vapour pressure of monoclinic sulphur (metastable) below the transition point.[2]

Above the transition point the rhombic form is the metastable phase and thus possesses the greater vapour pressure. The vapour pressure curve of rhombic sulphur above the transition point is represented by the dotted curve OR', which is a continuation of RO.

FIG. 9.   The S_8 molecule as seen parallel to and perpendicular to the axis of the puckered ring

[1] The curious fact that sulphur is oxidised more rapidly at 95·5° than at temperatures immediately below or *above* this point led Hedvall to believe that there is enhanced chemical reactivity at the transition point owing to the structural loosening of the crystal units. This is denied by Fishbeck, who maintains that the apparent enhancement is merely due to the natural difference in the reactivity of the two allotropes.

[2] The velocity with which monoclinic sulphur changes into the rhombic form increases as the temperature falls below 95·5°, reaching a maximum at about 35° and then decreasing (cf. pp. 36, 52).

The application of external pressure to a system at the transition point will necessarily cause a change in the transition temperature.   In the case of sulphur the transition temperature is raised when the pressure is increased, as shown by the curve *OC*.   If we know the heat of transformation and the densities of the two modifications we can calculate the effect of pressure
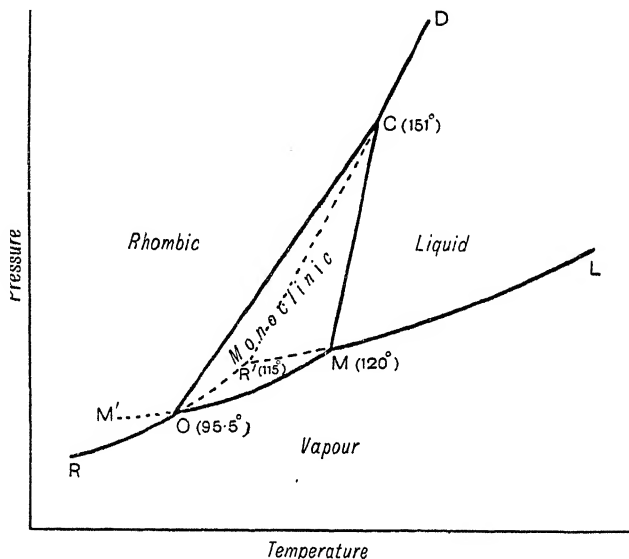
FIG. 10.   Equilibrium diagram of Sulphur

by means of the Clapeyron equation (p. 17).   Actually, the transition temperature is raised by 0·05° for each atmosphere increase in pressure.

In some respects the point *O* corresponds to the point *O* in the equilibrium diagram of water (Fig. 5).   It is, in fact, a triple point at which the three phases rhombic sulphur, monoclinic sulphur and sulphur vapour coexist in stable equilibrium.

At the point *M* (120°) monoclinic sulphur melts to a liquid and the curve *MC* shows the effect of pressure on this melting point.   The point *M* is also a triple point where monoclinic sulphur, liquid sulphur and sulphur vapour coexist in equilibrium.   The curve *ML* is the ordinary vapour pressure curve of liquid sulphur.

The two curves OC and MC intersect at the point C (151°), which is thus a third triple point where rhombic sulphur, monoclinic sulphur and liquid sulphur are in stable equilibrium in the entire absence of the vapour phase.

Metastable States.—When rhombic sulphur is heated above the transition point it is in a metastable condition, and it is perforce in this condition when it melts at 115°. Consequently, the liquid derived from it on fusion is also in a metastable condition. The point R' is thus a triple point in a metastable region and is fixed by the intersection of the prolongations of RO and LM. The curve $R'C$ shows the effect of pressure on the "metastable" melting point of rhombic sulphur. Finally, the curve CD (a continuation of $R'C$) represents the effect of pressure on the "stable" melting point of rhombic sulphur, since the possibility of transition into the monoclinic form ends at C.

The salient features of the diagram may now be summarised from the standpoint of the Phase Rule :

	Areas			
$ROCD$	.	.	. Rhombic	⎫ Applying the Phase Rule—
COM	.	.	. Monoclinic	
$DCML$	.	.	. Liquid	
$ROML$	.	.	. Vapour	

Systems represented by points in these regions are bivariant and both pressure and temperature can be varied independently without altering the number of phases.

	Boundary Lines		
(Brackets indicate metastable states)			
RO (OR')	.	. Rhombic/vapour	
OM (OM')	.	. Monoclinic/vapour	⎫ By the Phase Rule—
ML (MR')	.	. Liquid/vapour	$2 + F = 1 + 2,$
OC	.	. Rhombic/monoclinic	$F = 1.$
MC	.	. Liquid/monoclinic	
CD (CR')	.	. Rhombic/liquid	⎭

All these systems are univariant, and the pressure and the temperature can be varied, but not independently.

	Triple Points	
O	Rhombic/monoclinic/vapour	⎫ By
M	Monoclinic/liquid/vapour	$= 1 + 2,$
C	Rhombic/monoclinic/liquid	
	(Rhombic/liquid/vapour)	⎭

These systems are invariant, for neither the pressure nor the temperature can be varied in the slightest without altering the number of phases. For each triple point there are characteristic, immutable values for the temperature and pressure.

A remarkable feature in connexion with monoclinic sulphur is the limitation of its range of stable existence on all sides as a thermodynamic island. As may be seen from the diagram, it can only exist in the stable state between certain temperatures and pressures represented by the points O and C.

In the present discussion we have considered four separate phases, viz. rhombic sulphur, monoclinic sulphur, liquid sulphur and sulphur vapour. Is it possible for these four phases to exist together in stable equilibrium ? The Phase Rule supplies the answer, for the variance of such a system is given by—

This is an impossible value, and it is evident therefore that such a system of four phases is incapable of existing in true equilibrium.

28. The Molecular Complexity of Liquid Sulphur.—The element sulphur has the peculiarity that its melt is a complex liquid composed of different molecular species in dynamic equilibrium.

When sulphur is heated above the melting point it fuses to a pale yellow mobile liquid. On raising the temperature still further, the yellow liquid becomes dark brown and viscous. This behaviour led Alexander Smith to conclude that there are two forms of liquid sulphur, which he designated $S\lambda$ and S_μ. The low temperature form $S\lambda$ is a yellow mobile liquid, soluble in carbon disulphide, and is probably S_8. At about 200° the limpid melt changes into a red, highly viscous form. This is probably due to the breaking open of the S_8 rings to form irregular chains, which tangle with one another and give rise to a great increase in viscosity. In liquid sulphur the two forms exist in a state of dynamic equilibrium, as indicated by the equation [1]

$$S\lambda \rightleftharpoons S_\mu.$$
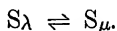
[1] Throughout the book half arrows are used to distinguish dynamic allotropy and isomerisation processes from phase reactions and dissociation processes.

The precise composition of liquid sulphur will depend on several factors, particularly the temperature and the rate of internal equilibration. According to Aten, molten sulphur contains a third molecular species, and this is denoted by the symbol S_π. This form is usually present in small amount only, and is soluble in carbon disulphide.

The case of liquid sulphur is one of *dynamic allotropy*, which does not involve an ordinary phase reaction. In ordinary allotropy one form is stable below and the other form stable above the transition point. The transformation of S_λ into S_μ is also reversible, but there is no definite transition point. Since the amount of each form present in the liquid depends on the temperature, the phenomenon is distinguished by the term *dynamic allotropy*.

If boiling liquid sulphur is suddenly cooled or quenched by pouring into cold water, the system is not given sufficient time

ACTION OF HEAT ON SULPHUR

	0°	120°	440°
State . .	SOLID	LIQUID	VAPOUR
Phenomenon	ALLOTROPY	DYNAMIC ALLOTROPY	DISSOCIATION

Changes: Rhombic $\underset{}{\overset{95°}{\rightleftarrows}}$ Monoclinic $_4 \underset{}{\gtrless} S_2$

Slow Crystallisation   Slow Crystallisation   Rapid Cooling

δ-SULPHUR   AMORPHOUS SULPHUR ⟵ PLASTIC SULPHUR
Hardens on standing
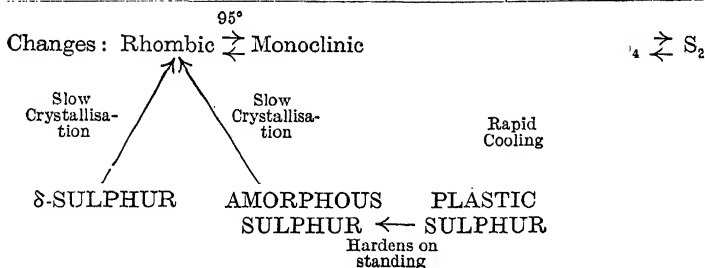
for equilibration or adjustment to the new conditions, and as a result, the rubber-like plastic variety of sulphur is produced. Even under these conditions, changes still go on in the material, and on standing, it slowly hardens to a yellow, brittle mass of amorphous sulphur.

When sulphur is produced in a chemical reaction, as frequently happens in the hydrogen sulphide group in qualitative analysis, the material is precipitated as a white, amorph-

ous powder, called δ-sulphur. The amorphous varieties of
sulphur are not to be regarded as allotropes, although, on
standing, they slowly crystallise into the stable rhombic
modification.

When liquid sulphur is boiled, the vapour is composed of
S_8 molecules, but at higher temperatures these dissociate into
S_4 molecules, and these again into S_2 molecules at elevated
temperatures.

The main features relating to the action of heat on sulphur
may be represented by the scheme shown on page 33.

Sulphur is indeed the chameleon of the elements and may
exhibit ordinary allotropy, dynamic allotropy, or gaseous
dissociation, according to the thermal environment.

In view of the complexity of liquid sulphur, certain reserva-
tions must be made with regard to the previous simplified
treatment of sulphur as a true unary or one-component
system. According to the Theory of Dynamic Allotropy pro-
posed by Smits, the three different molecular species may be
regarded as *pseudo-components*, so that liquid sulphur will
behave as a pseudo-ternary system. Unless we are quite
certain that the liquid has reached a stable state of internal
equilibrium, we are not justified in treating the system as
unary. The complete equilibria in the sulphur system are
thus complex, but although these complexities find no ex-
pression in Fig. 10, the salient features of the diagram still
retain their qualitative significance.

VI. TIN

Force, force, everywhere force. There is not a leaf rotting on
the highway but has force in it ; how else could it rot ?—
CARLYLE

29. **Tin Disease.**—The first observations of the tranforma-
tion of a solid element into another solid state appear to have
been made at a very remote period in the case of metallic tin,
and both Aristotle and Plutarch referred to the fact that this
metal suffers profound changes when subjected to intense
cold. These early observers were familiar with the collapse
of tin statues, and actually compared the process with that of
the melting produced by heat. Apart from these remarkable

conjectures, however, the phenomenon received little attention from a scientific standpoint.

The curious behaviour of the metal during severe spells of cold weather occasioned much surprise during the last century. It is recorded that the tin organ-pipes of the church at Zeitz, Germany, were ruined as a result of the cold weather experienced there in 1850. It is also known that a number of blocks of Banca tin, stored in the Customs House at Leningrad, crumbled to a powdery mass during the severe winter of 1867.[1] Fraud being suspected, the bars were returned to Rotterdam for investigation, but the analysis showed that the mass consisted of almost pure tin. The phenomenon is also noticed in museums, where tin medallions and coins sometimes become covered with wart-like patches of powdery grey tin. This is the so-called *tin disease, tin pest* or *tin plague.* If tin becomes afflicted with the disease, a rash of grey spots develops on the surface of the metal. The disease is contagious and can be propagated by inoculation. Once the sound metal is infected, it slowly but surely crumbles to a fine powder.

No explanation of the phenomenon was forthcoming until it was realised that the metal is capable of existing in different allotropic modifications. A careful study of the behaviour of tin at different temperatures has revealed that there are two allotropes of the element, viz. :

> grey tin or α-tin,
> ordinary tin, white tin or β-tin.

Grey tin has a cubic crystal structure while ordinary tin has a tetragonal structure. The third form of tin reported in the literature is not an allotrope.

30. **The Equilibrium Diagram.**—In Fig. 11, AB is the vapour pressure curve of grey tin or α-tin, BC the vapour pressure curve of white or β-tin, and CD is the vapour pressure curve

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[1] In a Memoir presented before the St. Petersburg Academy in 1870 Fritzsche relates : " The chief of a commercial firm informed me in February 1868 that many blocks of Banca tin had decayed in the store of the Customs House. I remembered dimly that some years previously large consignments of cast-tin buttons for military uniforms, kept in one of the Crown magazines, were found on inspection to have decayed into a shapeless mass. . . . From the very first, I had inclined to the opinion that the cause of the change in structure was the exceptionally low temperature at St. Petersburg during the winter of 1867-68. On January 26th the thermometer had gone down to $-38°$."

of liquid tin.   The two sublimation curves intersect at the
point B, which is the transition point of the system

<div align="center">grey tin   white tin.</div>

Below 18° grey tin is the stable form, and white tin cooled
below this temperature is in the metastable condition, as
indicated by the dotted prolongation of the curve CB.   It is
possible, however, to cool white tin much below this tempera-
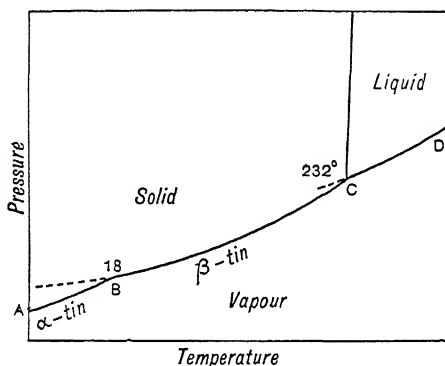
FIG. 11.   Vapour pressure curves of Tin allotropes

ture without apparent change, since the transformation into
grey tin takes place very slowly.[1]   It is well to note in this
connexion that the Phase Rule makes no stipulations with
respect to the speed of transformation of one phase into
another.   It tells us that the metastable phase will change
into the stable phase, but it does not tell us whether the
change will take a few seconds or a few days or a few thousand
years.   It affords, in fact, no information as to the duration
of the metastable state.

X-ray analysis has shown that the packing of the atoms in
the grey tin structure is of the diamond type, while that of
white tin belongs to the tetragonal system, as shown in Fig. 12.
The transformation of one phase into the other involves a
fundamental change in the space lattice of the crystal, and

[1] It would not be advisable to take tin utensils on a polar expedition,
since conditions in these regions would lead to fairly rapid disintegration
of the metal once the change had commenced.

this process takes place slowly owing to the manifestation of molecular lag or hysteresis. According to Ernst Cohen,[1] the maximum rate of transformation occurs at $-50°$, and it appears that the change is facilitated by the presence of electrolytes. In order to prepare a mass of grey tin, a mixture of white tin filings, some grey tin and a solution of an electrolyte is cooled to $-45°$ in a bath of liquid ammonia.
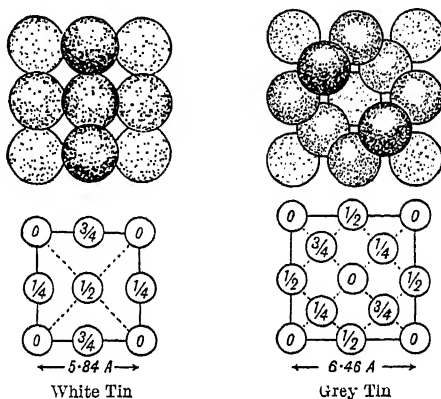
Fig. 12. Crystal structure of White Tin and Grey Tin (after Wyckof)

Numbers indicate the distances of the atoms above the plane of projection (in fractional parts of the length of the cube edge)

The effect of pressure on the transition point has not yet been determined experimentally, but the slope of the curve may be deduced from Le Chatelier's principle.

VII. PHOSPHORUS

Of allotropes of phosphorus forsooth there is no lack,
α-White, β-White, Violet and Black.—ANON

31. **Preparation of Commercial Varieties.**—The element phosphorus is commonly met with in the laboratory as white phosphorus and red phosphorus. The white variety is pre-

[1] *Physico-chemical Metamorphosis*, McGraw-Hill Book Company, Inc., New York, 1928.

pared commercially by heating calcium phosphate, sand and coke in an electric furnace :

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5,$$
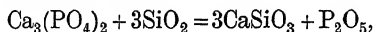
The phosphorus vapour is led away through a pipe and condensed under water. Red phosphorus is manufactured by heating white phosphorus to 250° out of contact with air in a porcelain or iron vessel provided with a safety-valve. The colour and vapour pressure of so-called red phosphorus depend on the temperature and the duration of heating. If the phosphorus is heated to a higher temperature for long periods, the material assumes a violet colour.

32. **The True Allotropes of Phosphorus.**—Pure *violet phosphorus*, which is sometimes called Hittorf's metallic

ALLOTROPIC FORMS OF PHOSPHORUS

	α-White	β-White	Violet	Black
1. Method of preparation	By heating calcium silicate, silica and carbon in electric furnace	By action of high pressure on α-white phosphorus	By cooling a lead solution of phosphorus	By compressing white phosphorus under 35,000 atmospheres
2. Crystal form	Cubic	Hexagonal	..	..
3. Density	1·85	1·8	2·3	2·7
4. Melting point	44·1°	..	590°	..
5. Ignition with match flame	Ignited	Ignited less readily	Not ignited	Not ignited
6. Electrical conductivity	Non-conductor	Non-conductor	Non-conductor	Conductor
7. Solubility in CS_2	Soluble	..	Insoluble	Insoluble

phosphorus, may be prepared by heating a solution of phosphorus in lead at 500° for 10 hours in absence of air. On cooling, the phosphorus allotrope separates from the lead in the form of violet crystals, and may be obtained in the pure state by dissolving away the lead with acids. Experiment shows that white phosphorus has a higher vapour pressure and a greater solubility in a given solvent than the violet form. In accordance with the rule of metastability (p. 21) this implies that white phosphorus is the less stable, or metastable form.

While investigating the effect of high pressure on ordinary or *hite phosphorus*, Bridgman discovered another allotropic

modification, which is called β-*white phosphorus*. The α- and β-white forms are enantiotropic (p. 45) with a transition point at $-77°$.

When white phosphorus is heated at $200°$ under a pressure of 12,000 kgm. per sq. cm., it is converted into yet another allotrope, which is called *black phosphorus*, but this change is irreversible. More recently, Bridgman obtained the black modification by compressing white phosphorus at ordinary temperature under a pressure of 35,000 atmospheres.

Some of the properties of the allotropes are summarised in the table on page 38.

33. The Equilibrium Diagram.—The equilibria between the various allotropic forms of phosphorus have been the subject of much research, and the main conclusions are embodied in Fig. 13.
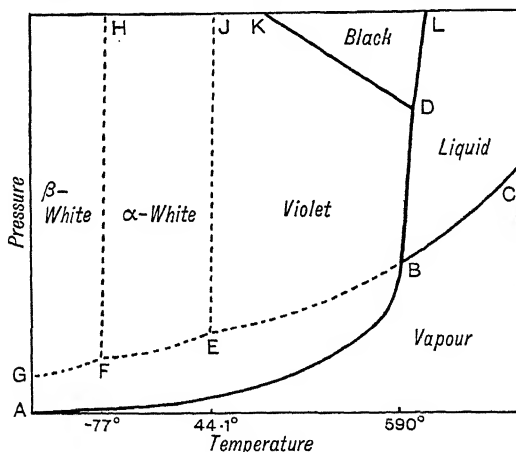
FIG. 13. Equilibrium diagram of Phosphorus

The curve AB is the vapour pressure curve of solid violet phosphorus ; it terminates at B, the melting point of the violet modification. The curve BC is the vapour pressure curve of liquid phosphorus ; it will end abruptly at the critical point. At the triple point B, the three phases, solid, liquid and vapour, will be in equilibrium. The effect of pressure on the melting point of violet phosphorus is represented by the curve BD.

The curve GF is the vapour pressure curve of Bridgman's β-white form. At the transition point F ($-77°$) this allotrope changes into the ordinary or α-white modification, and FH

represents the effect of pressure on the transition point.   The curve FE is the vapour pressure curve of ordinary α-white phosphorus with the melting point at E (44·1°).   At this triple point the three phases, α-white phosphorus, liquid and vapour, are in equilibrium, and the effect of pressure is shown by EJ.

It has been established by experiment that the two curves EB and BC are continuous.   Actually, therefore, we have to deal with one single curve EC, and this implies that molten white phosphorus is simply supercooled violet phosphorus. Accordingly, if we start with liquid phosphorus at the point C and cool it to the state represented by the point B, it may remain liquid and pass through the states represented by the points on BE, or it may be converted into violet phosphorus by assuming states represented by points on the curve BA.

The region of black phosphorus is represented by the area DLK.   The curve DL shows the effect of pressure on the melting point of black phosphorus, while DK indicates the effect of pressure on the transition point of violet phosphorus into black phosphorus.

34. **Red Phosphorus.**—Reverting now to the consideration of ordinary red phosphorus, we may recall that it differs from white phosphorus in physical and chemical properties as indicated in the following table :

	White Phosphorus	Red Phosphorus
1. Colour	White	Variable reddish-violet
2. Melting point	44°	Above 500°
3. Specific gravity	1·83–1·85	2·05–2·39
4. Smell	Garlic-like	Odourless
5. Solubility in CS_2	Soluble	Insoluble
6. Ignition temperature	30°	260°
7. Action of air	Phosphoresces owing to oxidation	No phosphorescence or oxidation
8. Action of chlorine	Combines at room temperature	Combines only when heated
9. Action of hot sodium hydroxide	Forms phosphine PH_3	No action
10. Physiological effect	Poisonous	Non-poisonous

When red phosphorus is heated to 360° out of contact with air, it sublimes and condenses in globules of the white modification. The nature of red phosphorus has been the subject of much speculation, but it is generally believed to be a solid solution or isomorphous mixture of white and violet phosphorus in dynamic equilibrium, as indicated in the scheme

<center>RED PHOSPHORUS</center>

$$P_{white} \qquad P_{violet}$$
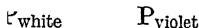
The precise composition of red phosphorus will depend upon the thermal treatment (temperature and time of heating) to which it has been subjected during its preparation.

VIII. CARBON

That diamonds as large and as pure as any that the Kimberley mines have brought to light will be produced in the laboratory is a moral certainty.—COLLINS

35. **The True Allotropes of Carbon.**—Although carbon exists in several familiar varieties, notably charcoal, graphite and diamond, it appears that there are only two definite allotropic modifications of the element in the solid state. Until recently, it has been customary to include charcoal and its " amorphous " variants among the allotropes of carbon, but the X-ray analysis of these materials has revealed that they are micro-crystalline and possess the graphite structure. A new unstable form of carbon, called *dicarbon* (C_2), has been prepared by Klemenc of Vienna by the controlled decomposition of carbon suboxide under low pressures :

$$C_3O_2 \qquad CO_2 \qquad C_2$$
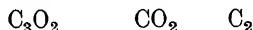
Dicarbon is a gas ; it polymerises to a purplish-red solid, which is soluble in water. The two common allotropes of carbon, however, are diamond and graphite, which have the space lattices shown in Fig. 14.

36. **The Structure of Diamond.**—Diamond forms crystals belonging to the cubic system, and the tetrahedral arrangement of the atoms is due to the quadrivalency of carbon. The structure (Fig. 14 (*a*)) also reveals an arrangement of atoms in rings of six, which is strangely reminiscent of the benzene

ring. As Sir William Bragg has pointed out, the renowned hardness of diamond is undoubtedly connected with this perfection of internal arrangement, each atom being bound with equal strength to four other carbon atoms by true chemical bonds or covalent links. The ability of diamond to scratch any other material is due to the circumstance that no other substance has atoms so firmly fixed in their places. In the

(a) Diamond   (b) Graphite
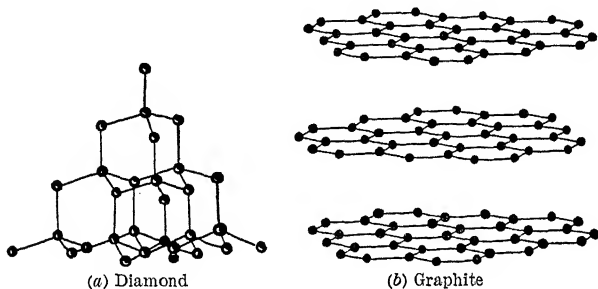
Fig. 14. Crystal structure of Diamond and Graphite

diamond the concept of a molecule has no significance, since the linking is extended in all directions to the limits of the crystal itself. In fact, the whole crystal may be looked upon as a single solid molecule, which the Germans picturesquely call a " giant molecule ".[1]

37. **The Structure of Graphite.**—Graphite, the second crystalline modification of carbon, has a hexagonal crystal, which consists of hexagonally-studded sheets of carbon atoms, as shown in Fig. 14 (b). The distance between any two carbon atoms in a sheet is slightly less than in the diamond but the distance between the sheets themselves is much greater. It is this peculiarity which gives to graphite its excellent lubricating properties, since one layer of atoms is able to slide freely over another layer like a chemical pack of cards. In other

[1] A new variety of diamond, called Type II, was discovered in 1934 by Sir Robert Robertson and his co-workers. It has the same essential structure as ordinary or Type I diamond, but the intensities of the X-ray reflexions are not the same. The ordinary diamond is very anisotropic between crossed nicols, while Type II is nearly isotropic. The rarer variety of diamond appears to be the normal type, inasmuch as its properties agree more closely with those predicted from theory. Since Type II does not show the strain bands exhibited by the ordinary diamond it has been suggested that the difference in properties is due to the strain to which the ordinary type has been subjected.

words, the bonds are strong in two dimensions, weak in the third, and this is the essential requirement of a good lubricant.

38. **Interconversion of the Varieties of Carbon.**—The inter-conversion of the different varieties of carbon is usually expressed by the scheme
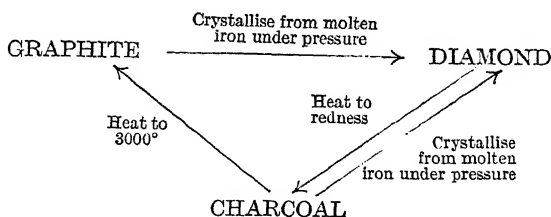
and there is now little doubt as to the essential validity of such a representation.

The diamond mines at Kimberley are the craters of extinct volcanoes, and it seems that the true matrix of the diamond is the so-called *blue-ground* or *kimberlite*, which has been forced up from below by volcanic action. Among other minerals it contains pieces of black shale, and it is this which supplied the raw material for the change into diamond by heat and pressure in the subterranean laboratory of the Earth. Geologists believe that diamonds were produced through the crystallisation of carbon from fused silicate magmas under enormous pressures, and Moissan's famous experiment on the synthesis of diamonds is frequently quoted in support of this contention. It may be recalled that Moissan packed a carbon crucible with iron and sugar-charcoal, heated the mixture to 4000° in the electric arc furnace, and then plunged the crucible into cold water. The sudden cooling brought about the immediate solidification of the outer layer of the iron, and since iron expands when it solidifies, the subsequent cooling of the enclosed liquid produced enormous pressure on the carbon as it crystallised from solution. After dissolving away the iron and removing the graphite particles, Moissan counted about a dozen diamond-like particles. The largest synthetic diamond $(2 \times 1 \times 1$ mm.) was made in 1936 by Hershey at McPherson College and the Bureau of Standards declare it to be a pure diamond of the first quality.

The heat of combustion of diamond is 7873 cals, and that of graphite 7832 cals per gram. Since the diamond structure

contains more energy than the graphite structure, it follows that diamond is the metastable form. The difference, however, is so slight that the transition of diamond into graphite is infinitely slow, and it is easy to understand why the spontaneous transformation of diamond into graphite has never been observed.

39. The Equilibrium Diagram.—Owing to the great experimental difficulties, the equilibrium diagram for carbon is largely hypothetical. When carbon is heated under atmospheric pressure it begins to volatilise at 3600° without liquefying. If, however, the heating were carried out under high
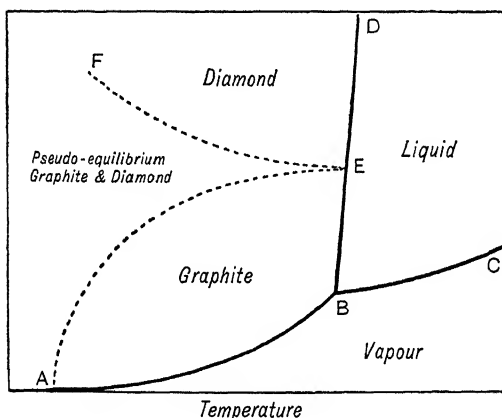
FIG. 15.   Equilibrium diagram of Carbon

pressure, it is probable that carbon would melt to a liquid and crystallise on cooling in the manner of ordinary liquids. As indicated previously, diamond is considered to be the metastable and graphite the stable form of carbon.

According to Tammann's diagram (Fig. 15), the vapour pressure of solid graphite is represented by AB, and it is supposed that carbon would melt at the point B, if the pressure were sufficiently high. The curve BD would indicate how the melting point of graphite would change with pressure.

The area AEF represents the region where the diamond is in a state of pseudo-equilibrium. The curve FE represents the temperature and pressure at which graphite is converted into diamond, and the curve AE the temperature and pressure for the reverse change of diamond into graphite.

According to this theory, solutions of carbon in fused magmas contain diamond and graphite in equilibrium. If the cooling of the solution is comparatively slow, graphite is produced, but if the cooling is extremely rapid, diamonds are formed.

IX. ENANTIOTROPY AND MONOTROPY

Every form as nature made it is correct.—PROPERTIUS

40. **Position of Transition and Melting Points.**—A substance is said to be *dimorphous* when it exists in two different crystal-

Temperature
(*a*) Enantiotropy

Temperature
(*b*) Monotropy
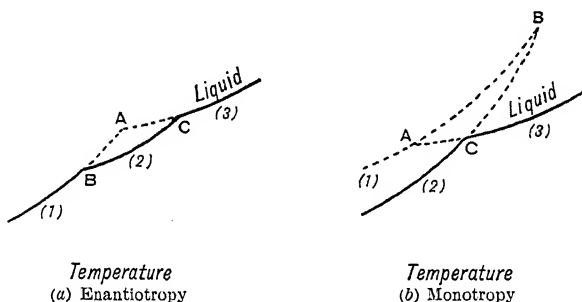
FIG. 16.   *pt*-curves for enantiotropic and monotropic substances

line forms. These dimorphous substances may be divided into classes according as—

(*a*) the transition point is below the melting point,
(*b*) the transition point is above the melting point.

When the transition point is below the melting point the two forms are said to be *enantiotropic*, and the phenomenon is called *enantiotropy* (from the Greek, meaning *opposite habit*). The essential equilibria which are observed in the case of enantiotropic substances may be represented on a *pt*-diagram, as shown in Fig. 16 (a).

In this diagram, curve (1) is the vapour pressure curve of the first modification, curve (2) that of the second modification, and curve (3) that of the liquid derived from the substance on fusion. The point *B* is the transition point, while *A* is the melting point of the first modification and *C* that of the second

modification. The behaviour is entirely analogous with that of the two forms of sulphur, which are of course enantiotropic. When, therefore, a substance exhibits enantiotropy, the transition point is below the melting point and is realisable under ordinary atmospheric pressure. Moreover, the two forms are stable and have a definite range of stable existence, and the change from one to the other is reversible. There are many other examples of enantiotropic substances, such as grey and white tin, and the red and yellow forms of mercuric iodide.

Enantiotropy	Monotropy
1. Transition point below m.p.	Transition point above m.p.
2. Transition point realised under atmospheric pressure	Transition point not realised under atmospheric pressure
3. Both forms stable	One form stable, other form metastable
4. Transformation is reversible	Transformation is irreversible
5. Slow heating changes first form at transition point into second form, which melts at higher temperature	Heating causes the metastable form to melt, and substance solidifies and re-melts at higher temperature
Examples : rhombic and monoclinic sulphur ; grey and white tin ; red and yellow mercuric iodide	Examples : α- and β-benzophenone; white and violet phosphorus ; graphite and diamond

When the transition point lies above the melting point the two forms are said to be *monotropic*, and the phenomenon is termed *monotropy*. Monotropic substances exist in two forms, one of which is metastable with respect to the other at all temperatures up to the melting point. The transition point cannot be realised under atmospheric pressure, and the change can take place in one direction only. In other words, the transformation of monotropic substances is irreversible. Moreover, the metastable form of a monotropic substance possesses higher vapour pressure, lower melting point and greater solubility in a given solvent than the stable modification.

The equilibria which occur in the case of monotropic substances are represented in Fig. 16 (b), where the previous notation has been employed. The point A is the melting point

of the metastable modification and C that of the stable form. Curve (1) is the vapour pressure curve of the metastable form, curve (2) that of the stable form and curve (3) that of the liquid. The transition point should lie at B, but this point cannot be reached under atmospheric pressure. As an example of a monotropic substance we may cite benzophenone $(C_6H_5)_2CO$. The metastable form of benzophenone melts at $26 \cdot 5°$, then solidifies, and re-melts at $48 \cdot 5°$, which is the melting point of the stable modification.

The chief differences between enantiotropy and monotropy are given in the table on page 46.

41. **Inversion of the Phenomena.**—The application of very high pressure may cause a considerable alteration in the nature of the equilibria between the two forms of a dimorphous substance, and it may happen that a monotropic substance becomes enantiotropic or an enantiotropic substance monotropic under the new conditions. At ordinary pressures, sulphur is enantiotropic, but if the pressure is raised above 1400 atmospheres it becomes monotropic, because the rhombic form alone is capable of stable existence under these conditions. It is evident, therefore, that the terms enantiotropy and monotropy are restricted in their application and it is necessary to specify the conditions under which the substance is enantiotropic or monotropic. To be precise, for instance, we should have to state that sulphur is an enantiotropic substance under ordinary pressure.

The inversion of enantiotropy and monotropy through the agency of high pressure is of frequent occurrence in nature and may account for those geological processes which cannot be duplicated with the pressures available in the laboratory.

X. THE PHENOMENON OF ALLOTROPY

> Those planetary systems far within,
> Atoms, electrons, whirling on their way
> To build and to unbuild our solid world.—ALFRED NOYES

42. **The Evolution of the Concept.**—The idea of a chemical element was advanced by Robert Boyle in 1661 and this retained its essential significance until the advent of sub-atomic chemistry. Towards the end of the eighteenth century Lavoisier recognised carbon as an element and again met with

it in the diamond, which he was able to convert completely into carbon dioxide. Soon after the publication of the Atomic Theory, Dalton came to the conclusion that the existence of the element carbon in such widely different forms, charcoal and diamond, presented an entirely new phenomenon. He sought to explain it by assuming the carbon to be in different states of aggregation, and although little further interest was shown in the matter, it became an accepted fact that this element can appear in two different forms.

When later it was recognised that compounds of the same composition may possess different chemical properties (isomerism), and that the same chemical compound can appear in different crystalline forms (polymorphism), the way was prepared for the general acceptance of the idea that a chemical element can also appear in different modifications. The analogy, however, was not complete until 1822, when Mitscherlich demonstrated that the element sulphur is able to crystallise in two forms, rhombic and monoclinic. Berzelius also showed that selenium assumes different states under different conditions. Finally, in 1841, after Schönbein had described the transformation of oxygen into ozone, Berzelius introduced the term allotropy and expressed himself as follows :

Under the influence of certain, as yet unascertained conditions, several elementary substances possess the strange property of assuming dissimilar external states or forms. . . . The earliest known example of such dissimilar forms is afforded by the different states of carbon in the diamond and in wood-charcoal or in ignited lamp-black. . . . Perhaps this is a characteristic of all elementary substances, although it has been observed up to the present only in the case of a small number. As yet, we can form no likely idea as to the cause of this difference in the properties of an elementary substance. We shall give the name *Allotropy* to this phenomenon and say that the elementary substance carbon is found in wood-charcoal and in the diamond in dissimilar allotropic states. The term is derived from the Greek, meaning *another shape*.

Clearly recognising the comprehensive character of the phenomenon, Berzelius counted among the allotropic states of an element not only those forms which differ merely in physical properties, but also those states which show different chemical behaviour. According to Berzelius, allotropy includes the chemical isomerism as well as the physical isomerism (polymorphism) of the elements, and on these premises, oxygen and ozone are to be regarded as allotropes.

These views were acceptable to the majority of chemists, including van 't Hoff, who wrote as follows :

The term *allotropy* refers to the phenomena of isomerism in the case of chemical elements irrespective as to whether they are caused by polymerism, as in the case of ozone (O_3) and oxygen (O_2), or by polymorphism, as in the case of rhombic and monoclinic sulphur.

There were some chemists, however, who did not subscribe to these views, and Lehmann, in particular, drew a distinction between allotropy and chemical isomerism. E. von Meyer, on the other hand, maintained that allotropy differs from polymorphism, since the former is accompanied by chemical differences, while the latter is associated with chemical identity. There were other authors too, notably Nernst and Arnold, who preferred to confine the term to the behaviour of elements in the solid state only.

Various theories have been proposed in order to account for the phenomenon of allotropy. According to the *Configuration Theory*, allotropy is due to a difference in the number of atoms in the molecule, as in oxygen and ozone, or to a difference in the spatial arrangement of the atoms, as in graphite and diamond. It is, however, quite sufficient to say that allotropy is due to a difference in the spatial arrangement, since this must be different if the number of atoms is different. When it was discovered that there is a change in the internal energy of an element during the conversion of one allotrope into another, allotropic modifications were defined as forms of the same element having different amounts of internal energy. But it is obvious again that this definition is merely supplementary to the Configuration Theory, since different configurations will perforce have different amounts of energy.

43. The Extended Theory of Allotropy.—Although conflicting opinions were expressed regarding the nature of allotropy, it was taken for granted that the term was to apply solely to the behaviour of elements. The break from the traditional view was initiated by Wilhelm Ostwald, who included under the term allotropy the transformation and transition phenomena of elements and compounds. Thus anhydrous sodium sulphate which exists in two crystalline or polymorphic forms
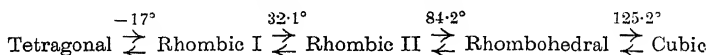
<div align="center">

234°

Rhombic Na_2SO_4 Monoclinic Na_2SO_4

</div>

and ammonium nitrate which exists in five polymorphic forms

Ammonium Nitrate

$$\text{Tetragonal} \underset{-17°}{\rightleftarrows} \text{Rhombic I} \underset{32\cdot1°}{\rightleftarrows} \text{Rhombic II} \underset{84\cdot2°}{\rightleftarrows} \text{Rhombohedral} \underset{125\cdot2°}{\rightleftarrows} \text{Cubic}$$

were considered to exhibit allotropy. The term is now understood to cover the physical and chemical isomerism of elements and compounds, as indicated in the scheme :

ALLOTROPY

Ordinary Allotropy   Polymorphism   Polymerism

ELEMENTS AND COMPOUNDS
Solids, liquids, gases

On this basis Smits of Amsterdam developed a comprehensive " Theory of Allotropy " according to which a so-called pure, one-component system may contain different kinds of molecules or molecular species, which are termed *pseudo-components*. It is assumed that an equilibrium can be established between the pseudo-components in virtue of reversible changes

α pseudo-component $\rightleftharpoons$ β pseudo-component,
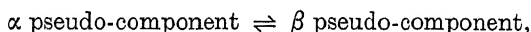
and that it is the speed of these changes, whether slow or rapid, which determines the essential behaviour of the system. It follows, therefore, that physical properties, such as melting point, boiling point, etc., relate not to a single molecular species, but to an *inner equilibrium* between molecules of different kinds. If, for some reason, the inner equilibrium is not restored we shall have an allotropic form.

There is at present no evidence to show that the forces which are operative in the building up of elements are in any way different from those responsible for the existence of isomers and polymorphs. Apart from the existence of co-ordinate linkages in the case of compounds, the manner in which the forces operate is probably the same, and there appears to be no fundamental reason why the term allotropy should not include the behaviour of both elements and compounds. In fact it has long been the practice of the leading chemical journals to use the term in its widest sense, and it is

only in this way that we can appreciate fully the essential significance of the phenomenon and view its several implications in their true perspective.

PRACTICAL METHODS

Experiment is the interpreter of Nature. Experiments never deceive. It is our judgment which sometimes deceives itself because it expects results which experiment refuses.— LEONARDO DA VINCI

1. **Determination of Freezing Point.**—There are two general methods of determining the freezing point of a pure liquid :

(i) by direct observation of the constant temperature of freezing ;

(ii) by determining the cooling curve from time-temperature observations.

For ordinary work with pure liquids, accurate determinations may be made by the first method, provided the following precautions are observed :

(a) the temperature of the cooling bath must not be too low, usually not more than 5° below the freezing point of the liquid ;

(b) the amount of supercooling should not exceed 0·5° ;

(c) the stirring should be efficient to ensure uniformity of temperature throughout the liquid.
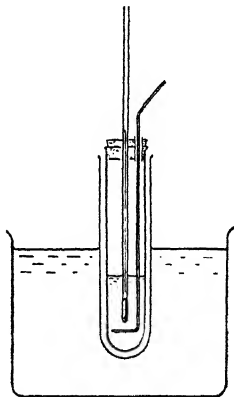
FIG. 17. Determination of freezing point

If, for example, the freezing point of benzene is to be determined, the liquid is introduced into a clean test-tube provided with a stopper carrying a standardised thermometer (graduated in tenths) and a short glass tube through which a glass stirrer may be worked, as shown in Fig. 17. The test-tube may be enclosed by a slightly wider tube to provide an air-jacket and thus ensure gradual cooling of the liquid when the apparatus is placed in the cooling bath of ice and water at 0°.

As the temperature falls, the liquid is stirred at a rate of one stroke per second and the stirrer allowed to click against the bottom of the vessel, since this is found to induce crystallisation when the freezing point is reached. More often than not, the temperature continues to fall a little below the freezing point owing to unavoidable supercooling. At this stage the liquid is stirred rather more rapidly until the mercury thread rises sharply and then remains steady at the freezing point. Owing to the evolution of latent heat the temperature now remains constant at the freezing point until all the liquid has solidified. Liquids which show strong supercooling may be " seeded " or inoculated with a small crystal of the solid in order to induce crystallisation.

For accurate work it is necessary to apply a correction for the exposed thread of mercury, since it is not at the same temperature as the immersed portion of the thermometer. For this purpose a second thermometer is supported alongside the main thermometer so that it records the temperature t_m of the middle part of the emergent thread. The corrected freezing point t_c is then given by

$$t_c = t_0 + 0 \cdot 000156 \; l \; (t_0 - t_m),$$

where t_0 is the observed reading and l the length in degrees of the exposed mercury thread.

2. **Rate of Formation of a New Phase.**—The transformation of a supercooled liquid into the solid phase depends upon two processes : (a) the rate of formation of nuclei, i.e. the number of crystallisation centres formed in unit time, and (b) the rate of crystallisation, i.e. the speed with which the nuclei grow to form crystals. The first process involves the gathering of the molecules to form centres of crystallisation, and from ten to a hundred molecules are usually necessary to form such a nucleus. Whether this nascent lattice structure breaks down again or forms a centre for the further assembling of molecules to build the crystal depends upon the experimental conditions. It can be shown experimentally that the rate of crystallisation of a supercooled liquid depends on the temperature.

The experiments of Tammann on the crystallisation of supercooled piperine (m.p. 129°) revealed that the speed increases with lowering of the temperature, reaches a maximum at about 40°, and then decreases as the temperature is lowered beyond this point, as indicated in Fig. 18.

These phenomena may be illustrated in the laboratory by measuring the speed of crystallisation of supercooled hippuric acid (m.p. 188°). For this purpose the substance is melted in a crucible or dish and the liquid sucked into previously warmed capillary tubes (15 cm. × 1 mm.). These are immediately quenched under the tap so that the liquid becomes a glassy solid. The glassy material may be kept for several days without showing signs of crystallisation. The speed of crystallisation at various temperatures can be measured by subjecting

Fig. 18.   Rate of formation of nuclei in a supercooled liquid

the tube to the specified temperature for four minutes and then counting the number of centres of crystallisation. In the case of hippuric acid it will be found that the maximum speed of crystallisation is attained at about 100°.
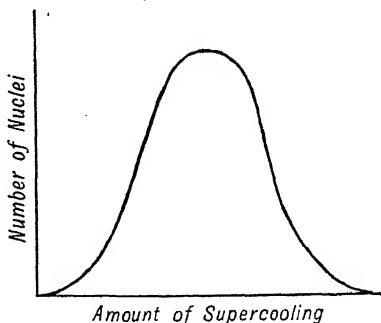
3. **Measurement of the Vapour Pressure of a Liquid.**—Several methods are available for determining the vapour pressure of a liquid, but we shall confine ourselves to a discussion of the simpler laboratory methods.

i. *The Barometric Method.*—This static method depends on the fact that a liquid introduced into the Torricellian vacuum above the mercury in a barometer tube gives off vapour and the pressure of the vapour causes the mercury to fall. When equilibrium is attained the extent to which the mercury is depressed is a measure of the vapour pressure of the liquid.
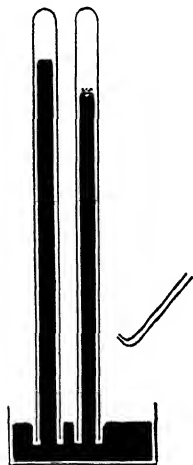

Fig. 19.   The barometric method

For the actual experiment two barometer tubes filled with mercury are placed side by side in the same trough of mercury, as shown in Fig. 19. By means of a bent pipette a small amount

of the liquid is introduced into the bottom of one of the barometer tubes and allowed to rise to the top of the column, where it is converted into vapour. More liquid is added if necessary, so that some of the liquid phase is seen above the mercury. This ensur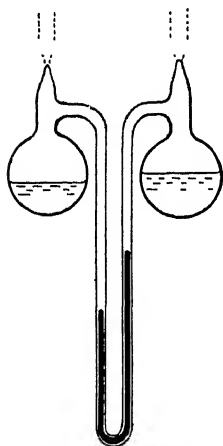es that the vapour is saturated. The fall in height of the mercury column as compared with the other barometer gives the vapour pressure of the liquid at the temperature of the experiment. Thus if B is the barometric pressure and h the height of the experimental column, the vapour pressure p is given by

$$p = B - h \text{ mm. Hg.}$$

To obtain reliable results the liquid must be perfectly pure and free from dissolved air. The barometers must also be carefully prepared with mercury from which dissolved air has been " boiled out " before use. Owing to these practical difficulties the barometric method is seldom used in this simple form.

Fig. 20.   Tensimeter for comparing the vapour pressures of liquids

ii. *The Differential Static Method.*— The vapour pressure of an organic liquid may be easily measured by comparison with water in a tensimeter, as shown in Fig. 20. Mercury is introduced into the manometer while pure water is placed in one bulb and the organic liquid in the other. Air is removed from the apparatus by heating the mercury and boiling the water and the organic liquid while both limbs of the tensimeter are simultaneously evacuated by means of a pump. When the " boiling out " process is complete the tubes are sealed in the blow-pipe flame.

The tensimeter is placed in a thermostat at constant temperature and the difference in the level of the mercury in the manometer is observed by means of a cathetometer. The vapour pressure of water at this temperature is found from published vapour pressure tables, and it is thus a simple matter to calculate the vapour pressure of the liquid under investigation. The manometric reading in millimetres is added to the vapour pressure of water if the liquid has the higher vapour

pressure, or subtracted from this value if the liquid has the lower vapour pressure.

iii. *The Evaporation Method.*—This method was introduced by Ramsay and Young and is suitable as a laboratory experiment. The apparatus (Fig. 21) consists of four main units. The vessel A is the evaporator in which the liquid is converted into vapour, B is a trap for catching the condensed vapour, C is a mercury manometer or pressure gauge and D
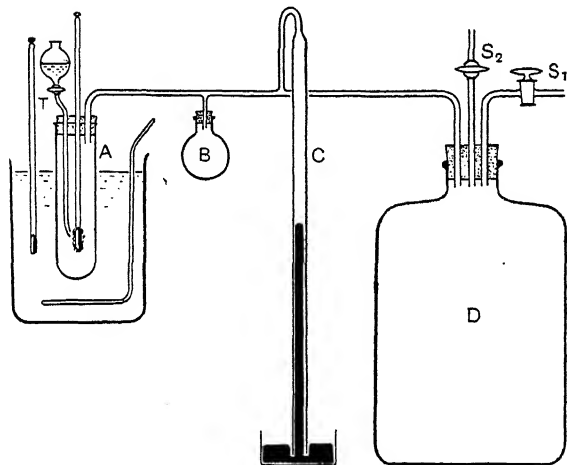

Fig. 21.   The evaporation method (Ramsay and Young)

is a large empty bottle which serves to increase the capacity of the system and thus minimise any errors due to leaks.

The evaporator A consists of a wide test-tube provided with a rubber stopper through which pass a thermometer and a small dropping funnel with a tap T and a lower delivery tube tapered and slightly bent so that it almost touches the thermometer bulb. The bulb of the thermometer is covered with a thin layer of cotton-wool for the purpose of retaining a film of the liquid in contact with the bulb. The evaporator is connected through the trap B with the manometer C and the vessel D, which communicates with the atmosphere via the stopcock S_2 and with a water-pump via the stopcock S_1.

After charging the dropping funnel with the liquid under investigation (e.g. chlorobenzene), the stopcock S_1 is opened to the pump and the pressure in the system reduced. The

apparatus is tested for leaks by closing S_1 and noting whether the mercury remains at a fixed height in the manometer. In this event the experiment is continued as follows.

The bath is raised to a convenient starting temperature, and, after closing S_1, a little of the liquid is admitted through the tap T and allowed to wet the cotton-wool around the thermometer. The thermometer will record a temperature lower than that of the bath and will, in fact, attain the temperature at which the vapour pressure of the liquid is equal to the pressure in the apparatus. This must be the case, for if the liquid is at a higher temperature, some of it will evaporate and cool the bulb, while if its temperature is lower, its vapour will condense and warm the bulb. When the temperature is steady the thermometer is read and the height of manometer noted. If $t°$ is the reading of the thermometer, h the height of mercury in the manometer and B the prevailing barometric pressure, we have

Vapour Pressure of Liquid at $t°$
$$= B - h \text{ mm. Hg.}$$
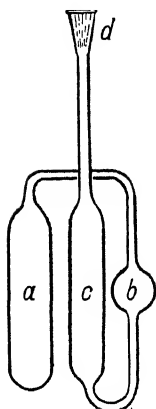
In order to obtain further readings a little air is admitted through the stopcock S_2 so that the mercury in the manometer falls about 5 cm. The temperature of the bath is raised until it is 5° higher than the previous reading of the cotton-covered thermometer, and the experiment is repeated by running in a little more liquid and noting the steady temperature and corresponding pressure indicated by the manometer. After repeating the observations at a series of higher temperatures, the vapour pressure readings are plotted against the corresponding temperatures in order to obtain the vapour pressure curve of the liquid.

FIG. 22. The isoteniscope

This method gives very reliable results, since the cotton-wool allows free evaporation around the thermometer bulb and thus prevents superheating of the liquid—the bane of vapour pressure and ebullioscopic measurements.

iv. *The Isoteniscope Method.*—A very convenient method due to Smith and Menzies[1] makes use of the *isoteniscope*, which, as its name implies, is an apparatus for indicating

[1] *J. Amer. Chem. Soc.*, 1910, **32**, 1412.

equality of pressure. The isoteniscope (Fig. 22) consists of a cylindrical bulb a joined to a small spherical bulb b and a cylindrical bulb c which terminates in a ground-glass joint d. If we wish to determine the vapour pressure of water, the bulb a is two-thirds filled with the liquid and attached at the ground-glass joint to the lower end of a short condenser B of the apparatus shown in Fig. 23. The upper end of the condenser is connected with a mercury manometer C and a large
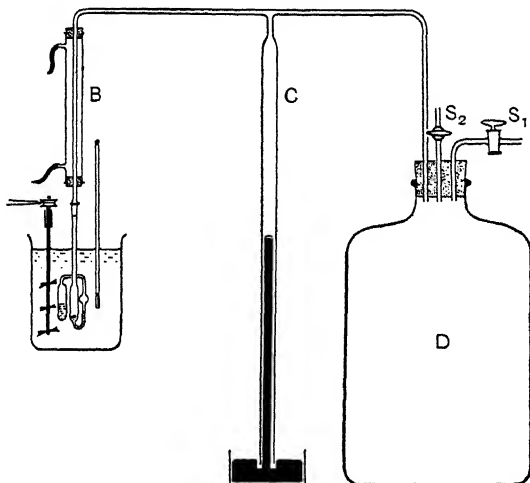

FIG. 23.   The isoteniscope method (Menzies)

bottle D provided with the stopcocks S_1 and S_1 for communication with a suction-pump and the atmosphere, respectively.

The isoteniscope is immersed in a bath of water or glycerol, which is vigorously agitated by means of a motor-driven stirrer. The bath is heated so that some of the liquid in the isoteniscope boils and condenses in the bent tube between the bulbs b and c. The preliminary " boiling out " is continued for a few minutes in order to remove all air from the liquid.

The burner is now removed from under the bath, and it is seen that the stream of bubbles still continues to pass through the liquid in the bend as the system cools. When, however, the liquid has cooled to the boiling point, the bubbling suddenly ceases and the liquid is sucked back towards the small bulb b. Immediately the liquid reaches the bottom of this

bulb, the pressure registered by the manometer and the temperature recorded by the thermometer in the vigorously stirred bath are read. We have therefore

Vapour Pressure of the Liquid at $t° = B - h$ mm. Hg.,

where B is the prevailing barometric pressure and h the height of mercury in the manometer.

The stopcock S_1 is now opened and suction applied by means of the pump. When the pressure in the system has been reduced by 5 cm. of mercury as indicated by the manometer, the stopcock is closed. The liquid in the isoteniscope boils again and bubbles of vapour continue to pass through the liquid in the bend. As the temperature of the bat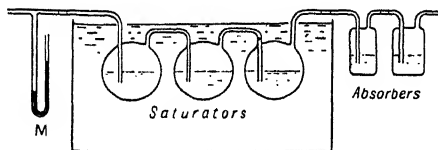h falls, a point is reached when the bubbling stops and the liquid is sucked back towards the bulb b as before. The temperature and pressure at which this occurs are immediately noted.

FIG. 24.   The air current method

Proceeding in this way with a cooling bath, the vapour pressures at a series of temperatures are determined, and the vapour pressure curve of water is finally obtained by plotting the observed pressures against the corresponding temperatures.

v. *The Air Current Method.*—This dynamic method is based on the principle that air saturated with the vapour of a substance will contain a volume of vapour proportional to the vapour pressure as expressed by the relation

$$\frac{\text{Vapour Pressure}}{\text{Total Pressure}} = \frac{\text{Volume of Vapour}}{\text{Total Volume}}.$$

The vapour pressure of a substance at a particular temperature can therefore be calculated if we know the total volume of the air, the total pressure and the amount of the vapour present.

The usual method consists in passing dry air through the liquid contained in a series of bubblers or saturators held at constant temperature in a thermostat. In the case of water the saturators shown diagrammatically in Fig. 24 are partly filled with the liquid and a slow stream of pure dry air is aspirated through the system so that the gas is completely

saturated with water vapour. The absorbers are charged with concentrated sulphuric acid to absorb the water vapour. After aspirating a known volume of air through the system under the pressure recorded by the manometer M, the absorbers are weighed. The increase in weight represents the amount of water vapour in the volume of air which has passed through the apparatus. These results and the above formula enable us to calculate the vapour pressure of water at the temperature of the experiment.

The method has also been applied to the measurement of the vapour pressure of solid iodine, the saturators being charged with crystals of iodine and the iodine vapour absorbed in a solution of sodium sulphite.

4. **Determination of Critical Temperature.**— A rough determination of the critical temperature of ether may be made by means of the apparatus shown in Fig. 25. A strong glass tube bent to U-shape is sealed at the shorter limb and partly filled with ether. Mercury is introduced, and after removing any ether which may have collected in the long limb the apparatus is sealed as shown.

FIG. 25.
Critical point
apparatus

The apparatus is suspended in an air-bath and viewed through a suitable peep-hole while the temperature of the bath is raised by means of a burner. As the temperature rises, the ether meniscus gradually flattens and then disappears suddenly at the critical temperature. Above this temperature the ether can exist only in the form of vapour. On cooling again to the critical temperature, a cloud or mist suddenly fills the tube, and when the mist settles, the original liquid layer is produced.

By measuring the compression of the air in the longer limb when the ether meniscus disappears at the critical temperature, the corresponding critical pressure can be calculated.

This experiment is not suitable for junior students owing to the risk of accident during the heating of the liquid under pressure.

5. **Preparation of the Allotropes of Sulphur.**—Natural brimstone is simply a compact form of rhombic sulphur. To obtain good crystals, however, the sulphur is dissolved in cold carbon disulphide (no flames !), filtered and allowed to evaporate very
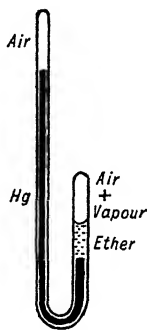
slowly in a covered flask. In this way the sulphur will be deposited in well-formed rhombic prisms.

The monoclinic form is produced by allowing molten sulphur to solidify. Some rhombic sulphur is melted in a crucible or beaker and allowed to cool. As soon as a solid crust is formed on the surface, it is pierced with a rod and the enclosed liquid run off by quickly tilting the crucible. It will be found that the inside of the crucible is lined with long, amber-coloured crystals of monoclinic sulphur. The monoclinic form cannot be kept for more than a few days, since each crystal becomes an opaque yellow mass of minute rhombic crystals.

The melting points of the two modifications can be determined in small tubes attached to a thermometer, which is immersed in a heated bath of sulphuric acid.

6. Interconversion of White and Red Phosphorus.—A small amount of white phosphorus is introduced into a small tube of strong glass which is then sealed in the blow-pipe flame. The tube is suspended in the neck of a small distilling flask containing diphenylamine, which boils at 310°. The organic liquid is then distilled and the high temperature causes the white phosphorus to change into the red variety. The transformation may be accelerated by the addition of a trace of iodine to the phosphorus.

A hard-glass test-tube is provided with a rubber stopper which is fitted with inlet and outlet tubes. A small quantity of red phosphorus is introduced into the tube and the air displaced from the apparatus by carbon dioxide. If the red phosphorus is now heated strongly out of contact with air, colourless drops of white phosphorus will distil on to the colder parts of the tube.

7. Preparation of Metastable Benzophenone.—The metastable form is obtained by the solidification of fused benzophenone in the complete absence of crystals of the stable rhombic form. It may be prepared by slowly passing air through a dilute alcoholic solution of benzophenone when the metastable modification is deposited in the form of transparent monoclinic crystals. These crystals fuse at 26° to a liquid which becomes solid again and does not melt until the temperature has been raised to 48°, the melting point of the stable form.

QUESTIONS

We ought to know what knowledge we possess
And be able to make it serve us in need.—LEIBNITZ

The average time allowed for answering each question is
30-40 minutes. When writing answers requiring diagrams
the student should never omit to specify what the axes of the
diagram represent. A well-executed diagram is meaningless
if the significance of the axes is not specified. Where possible,
it is also desirable to introduce sub-titles into the body of the
answer since this facilitates the marshalling of the facts, and,
too, the work of the examiner. Knowledge of the facts,
logical presentation and neatness are primary essentials, while
irrelevancy should at all times be avoided. Above all, the
student should have clearly in mind what is asked and what
should be given in the set time-limit.

1. Construct a diagram illustrating the connexion between
the phases of any pure substance, illustrating your answer by
reference to a particular case, and explaining the significance
of the different parts of your diagram.

(Associateship, Institute of Chemistry.)

2. Describe the allotropic forms of sulphur and discuss the
conditions governing their stability.

(Higher Certificate, Central Welsh Board.)

3. Describe the behaviour of sulphur on heating to its boiling
point. Under what conditions can the two chief crystalline forms
of sulphur be obtained ?

(Higher Certificate, Joint Matriculation Board.)

4. Distinguish between enantiotropic and monotropic sub-
stances and illustrate your answer by describing the characteristic
behaviour of one example of each class.

(Cambridge Higher School Certificate.)

5. In what respects does allotropy of sulphur differ from that
of phosphorus ? Describe the preparation and properties of the
two allotropic forms of phosphorus and explain how you would
prove that the two are different forms of the same element.

(Oxford and Cambridge Higher School Certificate.)

6. Explain, with examples, the meaning of the terms, *phase,
component, degrees of freedom, enantiotropy, monotropy* and *triple
point.* (B.Sc., Sheffield.)

7. Define the terms *allotropy* and *polymorphism.* Give a
short account of the properties of the two chief solid forms of tin
and phosphorus. (A knowledge of crystal forms is not required).

(Cambridge Higher School Certificate.)

8. Give an account of allotropy from the point of view of the Phase Rule. Illustrate your answer by considering the case of (*a*) sulphur and (*b*) phosphorus, giving the appropriate diagrams.
(B.Sc., London.)

9. What is the meaning and explanation of allotropy ? Illustrate your answer by reference to carbon, sulphur, phosphorus and oxygen.   (Higher Certificate, Central Welsh Board.)

10. What do you understand by the terms *polymorphism, allotropy* and *isomerism* ? Describe the properties of the two principal allotropic modifications of phosphorus and of sulphur. State in each case how the modifications can be changed, one into the other, and compare the conditions of transformation of the two elements.   (Fellowship, Institute of Chemistry.)

TWO-COMPONENT SYSTEMS

Where order in variety we see
And where, though all things differ, all agree.—POPE

44. **Method of Representation.**—For a system of two components in one phase we have from the Phase Rule

$$1 + F = 2 + 2,$$

so that the maximum variance is three. Accordingly, for the complete representation of the behaviour of a two-component system it would be necessary to employ a *ptc-* or space model with three axes at right angles to one another to represent respectively pressure, temperature and composition, as shown
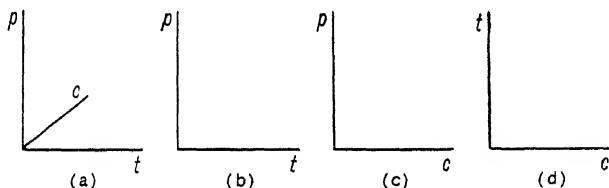

FIG. 26. The space or *ptc*-model (with *c* axis perpendicular to plane of paper) resolved into planar *pt-*, *pc-* and *tc*-diagrams

in Fig. 26. But space models of this kind are not well adapted for representation on the printed page and it is more convenient to use separate two co-ordinate diagrams to represent the relation between two of the factors while the third factor is fixed. In this way we have a *pt-*, a *pc-* or a *tc*-diagram which really comprises a section of the space model as shown in Fig. 26 (b), (c), (d).
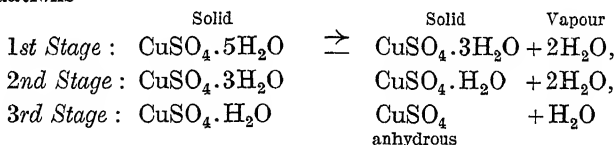
SOLID AND GAS PHASES

I. HYDRATES

> Nature never undertakes a change unless her interests
> are served.—MAX PLANCK

45. The Hydrates of Copper Sulphate.—Hydrated salts, which contain water in actual chemical combination or co-ordination with the salt, present several interesting features when viewed from the standpoint of the Phase Rule. As the components of the system it is customary to choose the anhydrous salt and water. The number of phases which they form may be large, inasmuch as each solid hydrate constitutes a separate phase. In general, a salt-hydrate dissociates on heating into a lower hydrate (or anhydrous salt) and water vapour. The equilibria in such systems are exemplified by the behaviour of the hydrates of copper sulphate.

Copper sulphate forms three well-known hydrates: (i) copper sulphate pentahydrate $CuSO_4.5H_2O$, (ii) copper sulphate trihydrate $CuSO_4.3H_2O$ and (iii) copper sulphate monohydrate $CuSO_4.H_2O$.[1] The dehydration of copper sulphate pentahydrate does not proceed in one step to the anhydrous salt, but in at least three different stages, as indicated by the equations

|	Solid		Solid	Vapour
1st Stage :	$CuSO_4.5H_2O$	$\rightleftharpoons$	$CuSO_4.3H_2O$	$+2H_2O$,
2nd Stage :	$CuSO_4.3H_2O$		$CuSO_4.H_2O$	$+2H_2O$,
3rd Stage :	$CuSO_4.H_2O$		$CuSO_4$ anhydrous	$+H_2O$

Each of these hydrates has its own vapour pressure, and, when two hydrates exist together, the observed vapour pressure is that of the higher hydrate.

Dehydration at Constant Temperature.—The dehydration of copper sulphate pentahydrate at constant temperature, i.e. isothermal dehydration, may be represented by a *pc*-diagram as shown in Fig. 27.[2] In the actual experiment the powdered

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[1] The existence of $CuSO_4.4H_2O$ is discussed on p. 71.

[2] The student should not confuse this process with the ordinary method of dehydrating copper sulphate crystals by raising the temperature. During *isothermal dehydration* the temperature is kept constant, while the pressure is lowered by means of a pump. During

crystals of pentahydrate are contained in a vessel provided with a pressure gauge. The apparatus is kept at 50° in a thermostat, while the water vapour is gradually removed from the system by means of a pump. With the pump in action it is found that the pressure remains constant at 47 mm., which is the value of the dissociation pressure of the pentahydrate. This behaviour is to be anticipated on the premises of the Phase Rule, since we have three phases present, viz.

$$CuSO_4.5H_2O,$$
$$CuSO_4.3H_2O$$
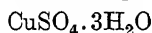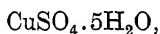
and vapour, so that

$$3 + F = 2 + 2$$
and $$F = 1.$$
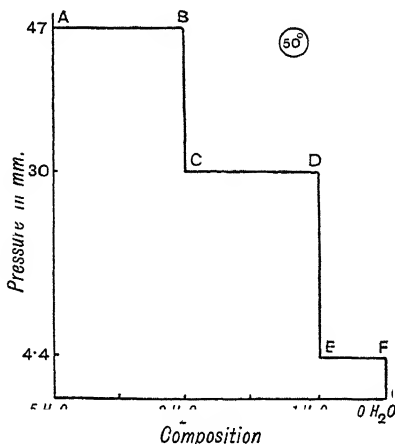
FIG. 27. Isothermal dehydration of $CuSO_4.5H_2O$

Along the line AB the system $CuSO_4.5H_2O/CuSO_4.3H_2O/H_2O$ is univariant and the pressure remains constant while the pentahydrate is being converted into the trihydrate. At the point B all the pentahydrate has been converted into the trihydrate, and since there is now but one solid phase the system becomes bivariant, as may be seen from the Phase Rule

$$2 + F = 2 + 2,$$
$$F = 2.$$

At this stage, therefore, we find a sharp drop in the pressure to 30 mm., the dissociation pressure of the trihydrate. Along CD the trihydrate is being converted into monohydrate, and since two solid phases are again present we have from the Phase Rule

$$3 + F = 2 + 2,$$
$$F = 1.$$

The system is thus univariant and the pressure remains

isobaric dehydration the pressure is kept constant while the temperature is raised. The ordinary dehydration of a substance by heating in a crucible is thus different from the process described above.

constant along CD. At D the conversion of the trihydrate is complete, and, since the system now contains monohydrate alone, it becomes bivariant and the pressure drops sharply along DE. When the pressure has been reduced to 4·4 mm. the monohydrate dissociates into the anhydrous salt, univariance is re-established and the pressure preserves a constant value along EF. When the monohydrate is entirely converted into anhydrous copper sulphate at F the system becomes bivariant, and, with the complete removal of water vapour from the system, the pressure drops to zero at G.

These and other studies of similar nature have led to the formulation of a very useful rule : *The step-wise change in dissociation pressure always indicates the formation of more than one definite, dissociating compound.* In the present case the alternation of univariance and bivariance corresponding to the step-wise change in the vapour pressure is a sure sign of the presence of more than one hydrate. The systematic measurement of the vapour pressure during the dehydration of a system thus affords a powerful method of detecting and ascertaining the properties of hydrates which cannot be prepared in other ways.

Rehydration at Constant Temperature.—The rehydration of anhydrous copper sulphate is accompanied by similar step-wise changes in the vapour pressure. If we start with anhydrous copper sulphate in an evacuated system as represented by the point G and allow water vapour to enter slowly, the pressure will rise along GF. At F the monohydrate is formed and the system immediately becomes univariant since two solid phases are now present. As more water vapour is being added to the system the pressure remains constant along FE until the anhydrous salt is completely changed into monohydrate. The conversion is complete at E, where the system reverts to bivariance and the pressure rises along ED until the trihydrate is formed at D. The presence of two solid phases renders the system univariant again and a constancy of pressure will be observed until the transformation into trihydrate is complete. With the disappearance of the monohydrate at C the system acquires another degree of freedom and the pressure rises along CB. When the pressure attains the value represented by B, the pentahydrate begins to be produced and the univariant system preserves a constant pressure until rehydration is complete at A.

46. **Temperature and Vapour Pressure of Hydrates.**—We may now compare the behaviour of a hydrate with that of liquid water. For the one-component system water/vapour we have $F = 1$; similarly, for the two-component system $CuSO_4.5H_2O/CuSO_4.3H_2O/H_2O$ we find $F = 1$. These two systems have the same variance and should therefore behave in analogous manner when subjected to changes of temperature.
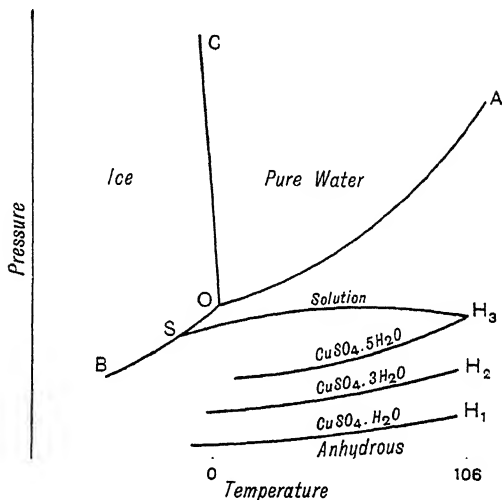

FIG. 28. Vapour pressure curves of hydrates

This prediction is fully substantiated by experiment and it is found that the vapour pressure curve of the hydrate system is of the same type as that of liquid water.

The actual equilibria may be expressed with reference to the water diagram as shown in Fig. 28. The curve BO is the vapour pressure curve of ice and OA that of liquid water, while OC represents the effect of pressure on the melting point. The curve H_1 is the vapour pressure curve of the monohydrate and shows that the vapour pressure rises with temperature. The curves H_2 and H_3 are the vapour pressure curves of the trihydrate and pentahydrate, respectively. The curve SH_3 gives the vapour pressures of saturated solutions of the pentahydrate at various temperatures and it lies below OA because the vapour pressure is lowered by the presence

of a dissolved substance. Moreover, since the solubility increases with the temperature the amount of substance in solution, and consequently the depression of vapour pressure, will be greater at higher temperatures, so that the curve for the solution will gradually recede from the water curve. The solution curve cuts the ice curve at the point S, where the four phases, ice, pentahydrate, solution and vapour, coexist in equilibrium. The Phase Rule predicts that this system is invariant, and the point is called a cryohydric point (p. 222). The curves for the lower hydrates have not been produced to meet the ice curve because these hydrates are not able to exist in contact with solution or ice.

When the pressure of water vapour is insufficient to produce the monohydrate, copper sulphate exists as the anhydrous salt in the region below the curve H_1. If the pressure is increased to a point on the curve H_1 the monohydrate is produced. The region of existence of the monohydrate lies between the curves H_1 and H_2—the curve H_1 indicating the pressure at which it can coexist with anhydrous salt, and the curve H_2 the pressure at which it can coexist with trihydrate. Similarly, the trihydrate region lies between the curves H_2 and H_3. The pentahydrate region is situated between the curve H_3 and curve H_3S, since this hydrate is able to exist in contact with ice. If the pressure of water vapour is increased above the values represented by the curve SH_3, the vapour may condense and form a solution. This solution of pentahydrate in water constitutes a new phase and its region of existence is confined by the pentahydrate curve H_3, the ice curve and the water curve. The point H_3, where the solution curve cuts the pentahydrate curve, occurs at about 106°. This is a transition point, where the pentahydrate breaks down or dissociates into trihydrate and saturated solution.

47. **The Application of the Term "Vapour Pressure".—** The distinction which must be drawn between the vapour pressure of a hydrate and that of a pure liquid or solution may possibly require some further elaboration. The vapour pressure of a hydrate is not any pressure of aqueous vapour with which it alone may be in equilibrium. It is clear from the Phase Rule that before the system can be univariant there must be present three phases, viz. two solid phases and the vapour phase. The usual term "vapour pressure of a hydrate" is a loose and rather misleading expression, for what we actually mean

is the vapour pressure of the system *Hydrate I|Hydrate II*
(or anhydrous salt). This second hydrate should in fact
be specified, since it sometimes happens that *Hydrate II* is
not produced, but *Hydrate III* instead. The vapour pressure
of the system *Hydrate I|Hydrate II* is not the same as that
of *Hydrate I|Hydrate III*, and it is necessary therefore to
specify which product of dissociation is present. The ordinary
custom of speaking of the vapour pressure of a hydrate is
without meaning unless the implicit assumption is made that
the next lower hydrate is formed, which is generally but not
always the case.

The significance of the term vapour pressure as applied to
pure liquid, solution and hydrate systems will be clear from
the following table :

THE SIGNIFICANCE OF VAPOUR PRESSURE

Character	Pure Liquid	Solution	Hydrate
1. Number of components	1	2	2
2. Number of phases	2	2	3
3. Degrees of freedom	$F = 1$	$F = 2$	$F = 1$
4. Compositions of phases	Invariable	Variable (concentration of solution can change)	Invariable
5. Definition of vapour pressure	It is the pressure of vapour with which it is in equilibrium	It is the pressure of aqueous vapour with which it is in equilibrium	It is the pressure of aqueous vapour with which it is in equilibrium in the presence of its next lower hydrate (or anhydrous salt)

48. **The Dynamics of Dehydration.**—Faraday was one of
the first to make a qualitative study of the speed of dehydra-

tion of a crystal hydrate. He noticed that a perfect crystal of sodium sulphate decahydrate retained its transparency for a long period when placed in a desiccator, whereas a crystal whose surface was scratched or damaged lost its water of crystallisation very rapidly and changed into the lower hydrate.

When copper sulphate pentahydrate is placed in a desiccator over sulphuric acid the break-down into the lower hydrate does not begin immediately, and there is a well-marked induction period during which there is no loss in weight. When the induction period is over and the change has commenced, the dehydration proceeds fairly rapidly until all the pentahydrate has been converted into the trihydrate. The induc-

FIG. 29. Dehydration nucleus in Copper Sulphate

tion period is a characteristic feature of the dehydration of all solid hydrates and its duration varies according to the character of the crystal and the conditions of the experiment.

The decomposition of a hydrate commences at minute centres, or *nuclei*, which grow into larger visible particles of the dehydration product. The rate of dehydration will thus be intimately connected with (a) the rate of nucleus formation and (b) the rate of growth of the nuclei. The formation of nuclei in hydrates has been studied by Garner of Bristol, who suspended the crystal from a quartz-fibre spring balance in an evacuated chamber and made visual or photographic counts of the nuclei. The nuclei are not spheres as was formerly supposed, and their shape depends on the lattice of the crystal in question. In the case of $CuSO_4.5H_2O$ they are star-like, as indicated in Fig. 29, but in $NiSO_4.7H_2O$ they appear as small discs. It is only in isotropic crystals like chrome alum that the nuclei are spherical. We do not know why the nuclei form at particular points in the crystal, but it is believed that they start on invisible scratches on the surface or at points where there are lattice discontinuities (Smekal cracks).

It will be evident that the over-all rate of dehydration will depend on the rates of three separate processes :

(a) rate of loss of vapour at the solid/solid interface between the two hydrates ;

   (b) rate of diffusion of vapour across the layer of dehydrated substance, which increases in thickness with time ;

   (c) rate at which the vapour leaves the external surface of the crystal.

The induction period, which is such a striking feature of dehydration phenomena, is supposed to be due to two factors : (1) the nuclei grow in a branching form through the lattice discontinuities or along the Smekal cracks, (2) an unstable intermediate product is first formed which acts as an auto-catalyst.[1]

   49. **Heating Curve of Copper Sulphate Pentahydrate.**—The behaviour of copper sulphate pentahydrate when it is slowly
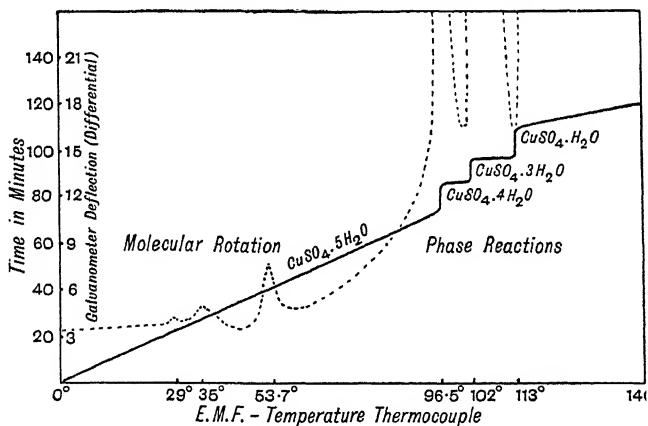
FIG. 30. Heating Curve of $CuSO_4.5H_2O$

heated from ordinary temperatures has been studied by the differential couple method.[2] One thermocouple is inserted in the finely powdered pentahydrate and balanced against a similar couple placed in powdered sodium chloride (which serves as standard since it suffers no phase changes on heating). The two systems are slowly heated in the same enclosure, while a third thermocouple registers the prevailing temperature. In this way very small thermal effects in the copper sulphate can be detected (p. 213).

[1] Garner, Symposium on "Reactions involving Solids," *Faraday Soc.*, 1938; Cooper, Colvin and Hume, *Trans. Faraday Soc.*, 1933, **29**, 576.
[2] Taylor and Klug, *J. Chem. Phys.*, 1936, **4**, 601.

When copper sulphate pentahydrate is examined in this manner, small heat effects are noted at 29°, 35° and 53·7° and these are believed to be due to the " water molecules " changing over from oscillatory to rotational motion.   At 96·5° dehydration occurs at constant temperature until one molecule of water is lost and there is left a residue of copper sulphate tetrahydrate, $CuSO_4.4H_2O$, as indicated in Fig. 30.   On heating further to 102°, the tetrahydrate loses a molecule of water and forms the trihydrate.   At 113° two molecules of water come off together and the trihydrate is converted into the monohydrate at constant temperature.   The fifth molecule of water is gradually lost as the temperature is further raised.[1]

These results definitely indicate the existence of $CuSO_4.4H_2O$, which has always been missed in the vapour pressure measurements.   This may be due to the circumstance that the vapour pressure of $CuSO_4.5H_2O/CuSO_4.4H_2O$ is very nearly the same as that of the $CuSO_4.4H_2O/CuSO_4.3H_2O$ system.   A more detailed examination of the vapour pressure relationships may make it necessary to modify the well-known pc-diagram (Fig. 27), but this cannot be done until actual vapour pressure data are available.

II. THE BEHAVIOUR OF SUBSTANCES IN THE ATMOSPHERE

I am the daughter of Earth and Water
    And nursling of the Sky,
I pass through the pores of the Oceans and Shores,
    I change, but I cannot die.—SHELLEY

50. **Atmospheric Water Vapour.**—Dry air consists for the most part of nitrogen and oxygen in practically constant ratio,[2] but the atmosphere surrounding the earth is charged with water vapour from the seas, lakes and rivers.   The maximum quantity of vapour which a given volume of air can hold at a given temperature is termed the saturation value at that temperature.   Such a condition would be attained if

[1] When the water of crystallisation comes off gradually as the temperature is raised, and not in the ordinary stepwise fashion, it is termed *zeolitic water*, since the zeolites behave in this way.

[2] At sea-level the chief gaseous constituents of dry air occur in the following percentage amounts by volume :

N_2	O_2	A	CO_2	H_2	Ne	He	Kr	X
78·03	20·99	0·93	0·03	0·01	0·0015	$0·0_35$	$0·0_55$	$0·0_66$.

we shook water and air in a flask for a period sufficient to ensure equilibrium. Normally, however, the atmosphere in the British Isles is only about two-thirds saturated. If p_a is the actual pressure of vapour and p_s the saturation pressure, the ratio p_a/p_s is termed the *humidity*.

Owing to the rotation of the earth the atmosphere experiences a diurnal cycle of temperature changes. During the daytime the temperature may be so high that the vapour in the atmosphere is less than the saturation value, but as evening comes the temperature falls, the air is cooled to the saturation point and the moisture is deposited in the form of dew. The temperature at which dew begins to be deposited in this way is called the *dew-point*. The amount of water vapour in the air can be found by using a hygrometer to determine the dew-point, or by measuring the increase in weight of anhydrous calcium chloride when a known volume of air is aspirated over it.

The condensation of vapour from the atmosphere is facilitated if dust particles are present to serve as nuclei around which the liquid droplets can form. Air which is almost free from dust particles can be cooled many degrees below the saturation point without condensation of water, and in this condition the air is said to be supersaturated with water vapour. When the air in the neighbourhood of the ground is cooled below the saturation point the condensation produces a *mist*. In large towns where there is a plentiful supply of soot particles the condensation gives rise to a more intense mist or *fog*.[1] *Clouds* are produced by the intermingling of almost saturated masses of air at different temperatures when one mass cools the other to the saturation point. If the fine droplets so formed grow sufficiently large, their weight will be able to overcome the viscosity of the air and they fall to the ground as rain. *Snow-flakes* are formed when the temperature at which the initial condensation occurs is below 0°, while *hail-stones* result from the freezing of rain-drops as they pass through layers of air at temperatures below the freezing point.

51. **Efflorescence.**—In the British Isles the pressure of water vapour in a well-ventilated laboratory is about 10 mm.

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[1] In the well-known C. T. R. Wilson Cloud Track Apparatus advantage is taken of the fact that moisture condenses on the ions which are produced when electrically charged particles fly through the gas. Each particle leaves a trail of ions upon which the water condenses and the track of minute droplets thus formed may be photographed.

at 15°. If the vapour pressure of a hydrate exceeds this value, the hydrate will lose water in the form of vapour, i.e. it will effloresce [1] on exposure to the atmosphere. A good example of an efflorescent substance is common washing - soda, $Na_2CO_3.10H_2O$, which gives off water vapour with the production of a lower hydrate, $Na_2CO_3.H_2O$. The change is invariably accompanied by the disintegration of the original crystal as indicated in Fig. 31. Once the change has commenced, hysteresis effects are overcome by the presence of nuclei of the transformation product, and the dehydration of the substance by the air proceeds rapidly until the decahydrate is entirely converted into the non-efflorescing monohydrate.
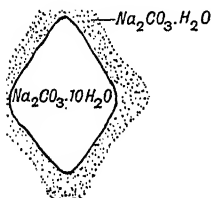
FIG. 31. Efflorescence

If the pressure of water vapour in the atmosphere is greater than the vapour pressure of the hydrate the substance will no longer effloresce. In fact, the behaviour of hydrates is essentially dependent on the climatic conditions, and more substances effloresce in Chicago than in Manchester.

52. **Deliquescence.**—When a substance forms a solution or liquid phase on standing in the air it is said to deliquesce.[2]

If calcium chloride or its common hydrate $CaCl_2.6H_2O$ is exposed to the atmosphere it absorbs water vapour and a solution of calcium chloride is ultimately formed. This is due to the fact that the vapour pressure of the hydrate is only 2·5 mm. and that of its saturated solution is only 7·5 mm. at ordinary temperature. This is considerably lower than the pressure of water vapour in the atmosphere, and the result is that a solution is formed which becomes progressively more dilute through the absorption of water vapour. The absorption process comes to an end when the vapour pressure of the solution is equal to the prevailing pressure of water vapour in the atmosphere.

It is important to note in this connexion that *all deliquescent substances are extremely soluble in water*. Indeed, the substance must be endowed with this great solubility if the solution is to

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[1] From *efflorescere*, to bloom, in allusion to the formation of a growth or crust on the surface of the crystal.

[2] From *deliquescere*, to melt or dissolve.

be so concentrated that its vapour pressure is lower than the pressure of water vapour in the ordinary atmosphere.

The vapour pressure relationships leading to efflorescence and to deliquescence are indicated in the following table :

BEHAVIOUR OF SUBSTANCES IN THE ATMOSPHERE

(Prevailing Pressure of Aqueous Vapour in the Atmosphere = 14 mm.)

| Substance | Vapour Pressure at 20° | | Behaviour |
	Hydrate	Saturated Solution	
$Na_2CO_3.10H_2O$	24·2	16·0	Efflorescent
$Na_2SO_4.10H_2O$	16·3	16·6	Efflorescent
$CuSO_4.5H_2O$.	5·1	16·0	{ Not efflorescent { Not deliquescent
$CaCl_2.6H_2O$.	2·5	7·5	Deliquescent
$NaOH.H_2O$.	Very low	1·0	Deliquescent

The decahydrates of sodium carbonate and sodium sulphate have a vapour pressure higher than the usual partial pressure of water vapour in the atmosphere and these salts are therefore efflorescent. Copper sulphate pentahydrate crystals do not usually effloresce, since the vapour pressure is lower than the atmospheric partial pressure. Moreover, the pentahydrate does not deliquesce because the vapour pressure of the saturated solution is higher than the pressure of water vapour in the air. Calcium chloride hexahydrate, however, has a very low vapour pressure, and, by absorbing water from the air, it forms a solution which also has a very low vapour pressure. The solution continues to absorb moisture until the vapour pressure is equal to the atmospheric partial pressure. The same process occurs with sodium hydroxide, which is extremely deliquescent owing to the very low vapour pressure of the solution. It is clear, therefore, that it is the low vapour pressure of the *solution* which determines deliquescence, and this in turn depends on the solubility of the substance. Actually, 74·5 grams of calcium chloride and 109·0 grams of sodium hydroxide will dissolve in 100 grams of water at 20°.

Other well-known deliquescent substances are potassium hydroxide and zinc chloride. Zinc chloride monohydrate, $ZnCl_2.H_2O$, is strongly deliquescent, but cadmium chloride dihydrate, $CdCl_2.2H_2O$, is efflorescent. Some organic substances

are deliquescent, and urea, though non-deliquescent in the ordinary air, is strongly deliquescent in an atmosphere saturated with water vapour. The deliquescence of certain salts is utilised in combating the dust nuisance on dry roads and hard tennis-courts in certain American towns. Calcium chloride is strewn over the area and allowed to deliquesce to a pasty film, which rapidly lays the dust.

53. Hygroscopic Substances.—A substance is said to be *hygroscopic* when it absorbs or adsorbs[1] moisture from the atmosphere. All deliquescent compounds are perforce hygroscopic, but there are many hygroscopic substances which absorb moisture without deliquescing. In fact most dry substances, especially if in a state of fine powder, are found to be hygroscopic.

The term is also applied to liquids, and strong sulphuric acid and absolute alcohol are well known for their hygroscopic properties. Pure heavy water, or deuterium oxide, is also hygroscopic in the sense that it absorbs ordinary water vapour from the atmosphere.

Both deliquescent and hygroscopic substances are extensively used for the drying of air and other gases. The relative efficiencies of some of the common drying agents, as listed in the International Critical Tables, are given below :

<div align="center">EFFICIENCY OF DRYING AGENTS</div>

(Residual H_2O signifies mgm. of water vapour left in 1 L. of a gas.)

Drying Agent	Residual H_2O	Drying Agent	Residual H_2O
P_2O_5	$< 2 \times 10^{-5}$	$CaCl_2$ (gran.)	0·2
$Mg(ClO_4)_2$	$< 5 \times 10^{-4}$	H_2SO_4 (95%)	0·3
KOH (fused)	0·002	$CaCl_2$ (fused)	0·36
H_2SO_4	0·003	$ZnCl_2$	1·1
NaOH (fused)	0·16	$CuSO_4$	1·4

Actually, the most efficient way to dry a gas is to pass it through a filter cooled in liquid air, since the vapour pressure of water is almost negligible at this very low temperature.

54. The Process of Drying.—Desiccators are widely used

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[1] In the process of *absorption* the whole body of the absorbent is active in taking up material, but in *adsorption* the process is more or less confined to the surface layers of the substance. Obviously, adsorption must precede absorption, and McBain has proposed the term *sorption* to cover both processes.

in the laboratory for removing moisture from substances and for preserving them in the dry state. In the ordinary form of desiccator used in analytical work (Fig. 32 (a)) the drying agent is introduced into the bottom part, while the material to be dried or preserved in the dry state is placed in an open vessel or watch-glass upon a porcelain plate or a perforated zinc sheet in the upper chamber. The desiccator is closed by means of a ground-glass lid which is lightly greased and pressed home until a transparent film of grease, free from air channels, is spread between the ground-glass surfaces. This film prevents the intrusion of moisture into the vessel while the drying agent is absorbing the water vapour inside the desiccator. The moisture on the surface of the solid in the upper chamber gradually diffuses into the surrounding air and

(a) Ordinary (b) Vacuum (c) Hempel
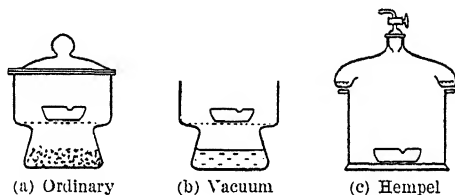
FIG. 32. Types of desiccators

is finally absorbed by the drying agent. The drying continues until the vapour pressure of the infinitesimal film of solution around the solid particles becomes equal to that of the drying agent. The intensity of the drying process is thus limited by the vapour pressure of the hydrate or solution which is formed in the lower chamber.

The speed with which a given substance is dried in a desiccator is governed by several factors : (a) the vapour pressure of the drying agent, (b) the temperature of the system, (c) the pressure in the system, (d) the active surface or superficial area of the absorber and (e) the position of the absorber with reference to the material to be dried.

The vacuum desiccator (Fig. 32 (b)) is provided with a stopcock, so that the air can be removed by means of a suction pump. In the rarefied atmosphere thus produced, the rate at which the water molecules leave the surface of the solid is greatly increased and they have, moreover, a practically free passage to the drying agent. As a result, the drying of

materials in a vacuum desiccator is about six times more rapid than in the ordinary type. In the Hempel desiccator (Fig. 32 (c)) advantage is taken of the fact that moist air is lighter than dry air. Moist air will tend to accumulate in the upper part of the desiccator, and the drying will naturally proceed more rapidly if the drying agent is placed in a trough in the upper chamber.

Air-drying plants are used in many industries in which the materials or manufacturing processes are affected by the dampness of the air. The air is circulated by means of a motor-driven fan through a bed or column of silica gel. Silica gel is a dry granular material, which is capable of adsorbing large quantities of moisture from the air. The water vapour is adsorbed in the capillary pores of the gel, and since the spent adsorbent may be reactivated by heating, it may be used over and over again.

Drying of Organic Liquids.—Organic liquids or solutions in organic solvents are usually dried by allowing them to stand in contact with a solid drying agent in a stoppered flask for several hours. The drying agent should remove only water and not react with the solvent or solute. *Calcium chloride* is much used for this purpose but it cannot be used for drying alcohols, phenols and amines. Anhydrous *sodium sulphate* removes water in virtue of the formation of the decahydrate $Na_2SO_4 \cdot 10H_2O$, but since the decahydrate breaks down at $32 \cdot 4°$ with regeneration of water, the anhydrous material cannot be used for drying above this temperature. *Phosphorus pentoxide* is a very powerful desiccant for use with inert solvents, but it cannot be employed with alcohols or basic substances. *Magnesium perchlorate* should never be used for drying alcohols owing to the formation of highly explosive alkyl perchlorates. The use of *sodium* for drying organic liquids depends on the actual decomposition of the water with evolution of hydrogen. Certain organic liquids, such as ethyl alcohol, may be dried by the *azeotropic elimination* of the water as part of a constant boiling mixture (p. 251).

55. **Fuming Liquids.**—Liquids which fume in the air give off vapour which unites with the water vapour to form a mixture having a vapour pressure greater than that of water. Although dilute hydrochloric acid does not fume, the concentrated liquid gives off hydrogen chloride which unites with the water vapour in the atmosphere. The air soon becomes

saturated with it and the mixture condenses in the form of a cloud or mist which we observe as fumes. Fuming thus depends on the nature of the liquid and the condition of the atmosphere in the vicinity. Even concentrated hydrochloric acid does not fume in the dry atmosphere of a desiccator.

Hydrobromic acid and hydriodic acid behave in the same way. Inorganic halides such as antimony pentachloride and organic derivatives such as benzoyl chloride also fume in the air owing to partial hydrolysis and the formation of gaseous hydrogen halide. It is for this reason that these substances have strong lachrymatory properties and cause copious watering of the eyes.

III. AMMINO COMPOUNDS

56. **Silver Chloride-Ammonia Compounds.**—Faraday discovered that dry silver chloride readily absorbs ammonia gas. When ammonia is passed over silver chloride the gas is absorbed and addition compounds or co-ordination derivatives are formed whose composition depends on the conditions of the experiment. The following compounds are known : silver monammino - chloride $(AgCl.NH_3)$, silver sesquiammino-chloride $(2AgCl.3NH_3)$ and silver triammino - chloride $(AgCl.3NH_3)$. These substances are solids which dissociate on heating in accordance with the following equilibria :

$$2(AgCl.3NH_3) \qquad (2AgCl.3NH_3) + 3NH_3,$$
$$(2AgCl.3NH_3) \qquad 2(AgCl.NH_3) \quad + NH_3,$$
$$(AgCl.NH_3) \qquad AgCl \qquad + NH_3.$$
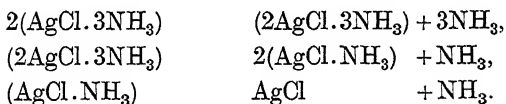
In each of these systems we have two solid phases and the gas phase. Putting $P = 3$ and $C = 2$, we find from the Phase Rule that $F = 1$. Since the system is univariant, each temperature must correspond to a definite pressure of dissociation. This " dissociation pressure " (cf. vapour pressure) will be constant at each particular temperature irrespective of the relative amounts of the phases. It is essential, however, that two solid phases be present as well as the gas phase if the univariant character of the system is to be preserved.

Let us suppose that the silver chloride is contained in an evacuated vessel provided with a delivery tube for introducing ammonia and with some form of manometer for registering

the pressure in the system as shown in Fig. 33. The apparatus is maintained at a suitable constant temperature by means of a thermostat. The behaviour of the system during the introduction of ammonia may be represented by a pressure-composition diagram as shown in Fig. 34.
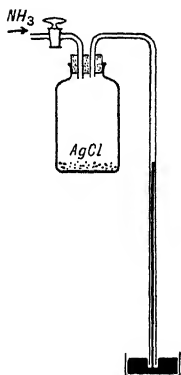
As the gas is introduced into the apparatus the pressure registered by the manometer will increase as indicated by the line AB. Along AB the system contains AgCl and NH_3, and by the Phase Rule $2 + F = 2 + 2$, so that the system is bivariant. At B the new compound ($AgCl.NH_3$) begins to be formed and since there are now three phases, we have from the Phase Rule $3 + F = 2 + 2$, so that the system is univariant. During the conversion of AgCl into ($AgCl.NH_3$) the pressure remains at a constant value along BC in accordance with the predictions of the Phase Rule.

FIG. 33. Absorption of NH_3 by AgCl

At the point C all the silver chloride has been converted into ($AgCl.NH_3$) and this compound is now the only solid phase. According to the Phase Rule, therefore, the system at this stage is bivariant and the further introduction of ammonia will cause the pressure to rise along CD. At the point D the pressure reaches the value at which the new compound ($2AgCl.3NH_3$) is formed, and as soon as some of this new solid phase is produced, the

FIG. 34.   Dissociation pressures of Ammino compounds

system loses its bivariant character and assumes the univariant state. The pressure will thus remain constant along

DE until the compound (AgCl.NH₃) is completely converted into (2AgCl.3NH₃).

When the conversion is complete the system again becomes bivariant and the pressure rises along *EF* until it reaches the value necessary for the formation of the compound (AgCl.3NH₃). During the conversion of the previous solid phase into the new phase the pressure remains constant as indicated by *FG*. As in the case of the hydrate systems it is important to note that the changes of pressure which occur on passing from one system to the next are abrupt, as demanded by the Phase Rule.

Dissociation of Ammino Compounds.—The changes are also abrupt when ammonia is gradually removed or pumped off from the system at constant temperature. Starting with a system represented by the point *G*, the pressure will remain constant so long as the two solid phases (AgCl.3NH₃) and (2AgCl.3NH₃) are present. With the disappearance of one solid phase at *F*, there is a sharp drop to the dissociation pressure of the next system, and along *ED* the two phases (2AgCl.3NH₃) and (AgCl.NH₃) are in equilibrium with the gas phase. The pressure now remains constant until the conversion of the one solid phase into the other is complete, when there is a further drop in the pressure to correspond to the system (AgCl.NH₃)/AgCl along *CB*. Finally, with the complete removal of ammonia from the system the pressure drops to zero at *A*. As pointed out previously, this step-wise change in the dissociation pressure always indicates the existence of more than one definite compound.

PRACTICAL METHODS

8. Determination of the Vapour Pressure of Hydrates.—The first attempt to measure the vapour pressure of a hydrate was made by introducing the crystals into the Torricellian vacuum above the mercury in a barometer tube and noting the depression caused by the vapour from the hydrate. This apparently simple method suffers from several defects, and is never used in this simple form. We shall therefore describe three more reliable methods, which serve also to illustrate the essential character of the equilibria in these systems.

i. *The Tensimetric Method.*—This method involves the

measurement of the difference in vapour pressure between the
hydrate system and liquid water contained in the two limbs of
a tensimeter. A modern form of tensimeter [1] is shown in
Fig. 35.

The tensimeter is first cleaned with chromic acid solution,
washed with pure water, steamed and then dried by heating.

FIG. 35.   Modern
tensimeter

The mercury used as manometric liquid is
purified by washing with nitric acid and
with water, and finally by distillation in
vacuum. The hydrate must also be puri-
fied by repeated crystallisation before use.

After introducing pure mercury into
the manometer M and pure water into the
bulb A, the side-tube is sealed off at the
point a. The pure dry hydrate is now
introduced into the bulb B, and the tensi-
meter then held in a horizontal position
so that the mercury collects in the aux-
iliary bulb C. The tube b is connected
to a suction-pump and the pressure in the
apparatus reduced to about 3 mm. The
mercury, the water and the hydrate are
then heated to remove all air, and the
whole system washed out with water
vapour generated in the bulb A. When
the air has been displaced by water
vapour in this way, the hydrate is heated

rather more strongly in order to start the dehydration, and the
side-tube is finally sealed at b. In the case of copper sulphate
the bulb B will now contain the system

$$CuSO_4.5H_2O/CuSO_4.3H_2O/vapour.$$

The apparatus is placed vertically in a thermostat at a
fixed temperature $t°$ for about a week in order to ensure the
attainment of true equilibrium. The difference in level of the
mercury in the manometer is accurately read by means of a
cathetometer. Since the vapour pressure of water at $t°$ can
be found from the vapour pressure tables, we have

V.P of Hydrate at $t°$ = V.P of water − h mm.,

where h is the difference in level of the mercury in the tensi-
meter.

[1] Carpenter and Jette, *J. Amer. Chem. Soc.*, 1923, **45**, 578.

ii. *The Vapour Balance Method*.—This method [1] consists in using a balance to find the mixture of sulphuric acid and water which has the same vapour pressure as the hydrate system. If the sulphuric acid is too strong the hydrate will give up water vapour and lose weight ; if the acid is too weak the hydrate system will take up water vapour and gain weight. The experiment thus resolves itself into finding the particular sulphuric acid solution which does not cause a gain or a loss in the weight of the hydrate system.

The apparatus employed is illustrated diagrammatically in Fig. 36. It consists essentially of a desiccator which is closed by an air-tight lid provided with two collars. Through one collar a combined fan and stirrer is operated by means of a motor, while the other collar is provided with a long glass tube for transferring the acid to a pyknometer or density bottle. From the underside of the lid a small sensitive balance with aluminium pans is suspended so that the diffusion fan rotates above one of the pans.

The measurement of the vapour pressure of copper sulphate pentahydrate is conducted as follows. About 5 of the pentahydrate
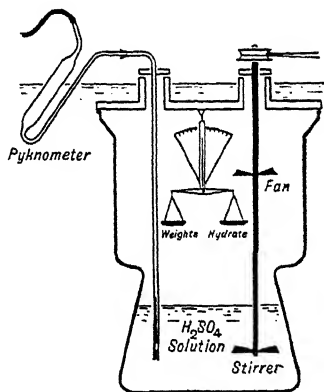
FIG. 36. Vapour balance method

crystals are weighed out and ground to a powder. The substance is heated to convert about half of it into the lower trihydrate. The hydrate mixture is spread out on the pan near the fan and counterbalanced with weights in the other pan. The fan and stirrer are now set in motion in order to accelerate the diffusion of vapour between the salt and the acid in the lower chamber.

After an hour or so the balance will show whether the hydrate system is gaining or losing water vapour. If the hydrate is gaining weight, more concentrated sulphuric acid is added to the solution in the lower chamber ; if the hydrate is losing weight, the solution is diluted by adding water.

[1] Wilson, *J. Amer. Chem. Soc.*, 1921, **43**, 719.

. When the concentration of sulphuric acid has been so adjusted that the salt preserves a constant weight after the fan has rotated for several hours, some of the acid is sucked into the pyknometer and its density determined. The vapour pressure of this particular solution is then found from the tables for sulphuric acid solutions. This is also the value of the vapour pressure of the hydrate system at the same temperature.

The determination takes about a fortnight, but it is claimed that the method is capable of great accuracy. In any case, the approach to equilibrium conditions from both sides and the direct comparison with sulphuric acid solutions of accurately known vapour pressure are commendable features of the method.

iii. *The Air-Current Method*.—This method, sometimes called the Transpiration method, involves the determination of the water removed from the hydrate by a slow current of dry air. For this purpose a known volume of dry air is slowly aspirated through a long U-tube charged with the hydrate and placed in a thermostat at a constant temperature. After leaving the U-tube, the air is passed through an absorption apparatus consisting usually of a small U-tube charged with calcium chloride and phosphorus pentoxide. The increase in weight of the absorption apparatus gives the amount of water in the volume of air which has passed over the hydrate, and from this we may readily calculate the vapour pressure.

Instead of measuring the volume of air, Partington [1] improved the method by passing air over the hydrate and through water at the same temperature. If w_H and w_W are the weights of water collected from the hydrate and from liquid water at the same temperature, we have

$$p_H = \frac{w_H}{w_W} \cdot p_W,$$

where p_H and p_W are the vapour pressures of the hydrate and water, respectively.

9. **To Measure the Absorption of NH$_3$ by AgCl.**—A known weight (0·1 g.) of dry, finely powdered silver chloride is sealed up in a thin-walled glass tube or ampoule, which is then placed in a bottle fitted with a glass stopper and connected to a gas-burette by means of lead tubing.[2] The bottle is filled with

[1] *J. Chem. Soc.*, 1911, **99**, 467 ; 1923, **123**, 160.

[2] Rubber tubing absorbs ammonia. The lead tubing may, however, be fixed to the glass by means of hard sealing-wax.

ammonia (previously dried by means of lime), and mercury is introduced into the gas-burette. The bottle is supported in a thermostat, the mercury levelled off after equilibration, and the volume of gas noted.

When the glass ampoule is broken by shaking, there is rapid absorption of ammonia, and when the process is complete, mercury is added to bring the system to atmospheric pressure. The difference between the two readings gives the volume of gas absorbed by the silver chloride at the temperature of the thermostat and the prevailing barometric pressure. Actually, at $20°$ and 760 mm., $0 \cdot 1$ g. of silver chloride absorbs nearly 23 c.c. of ammonia in the course of 30 minutes. This corresponds to the formation of the compound $(2AgCl.3NH_3)$.

QUESTIONS

1. Discuss in detail the question of the vapour pressure of salt hydrates, illustrating your answer by means of a Phase Rule diagram for a typical case (e.g. copper sulphate).

(B.Sc., Edinburgh.)

2. State the Phase Rule and explain the terms used. Discuss the aqueous vapour pressures of hydrated salts from the standpoint of this rule and indicate the conditions governing efflorescence and deliquescence.   (Associateship, Institute of Chemistry.)

3. Describe in terms of the Phase Rule the use of measurements of gas or vapour pressure to investigate the nature of (a) the hydrates formed by a salt and (b) the oxides formed by a metal. Outline the experimental method used for these and indicate the experimental and theoretical difficulties encountered in work of this kind.   (B.Sc., Special, Reading.)

4. Describe the methods by which the vapour pressures of salt hydrates have been determined, and discuss the results obtained.   (B.Sc., Sheffield.)

CHAPTER IV

DETERMINATION OF TRANSITION POINTS

Let the imagination go, guarding it by judgment and principles, but holding it in and directing it by experiment.
—FARADAY

57. **Principles of the Methods.**—We have already seen that the transition temperature of polymorphic substances is a perfectly defined point in accordance with the predictions of the Phase Rule. A similar behaviour is observed in the case of hydrates and other double salts, where one system is stable below a certain temperature and another system above it.

The transition temperature may be determined from observations of any suitable physical property. The methods fall roughly into two classes according as the observations relate to properties connected with the change in character of the crystal or to properties associated with the attainment of equilibrium between the two systems at the transition point :

CRYSTAL CHANGE

Volume Change	Thermal Change	Light Absorption Change	Lattice Change
Dilatometric method	Thermometric method	Optical method	X-ray method

ATTAINMENT OF EQUILIBRIUM

Same Vapour Pressure	Same Solubility	Same Conductivity	Same E.M.F.
Vapour Pressure method	Solubility method	Conductivity method	E.M.F. method

At the transition point the two forms of a single substance or the two hydrates are in equilibrium, which implies that they have the same vapour pressure, the same solubility and the same electrical conductivity in saturated solution. For similar reasons saturated solutions of the two hydrates will show no electromotive force when brought into contact at the transition temperature.

58. **The Experimental Methods.**—The determination of the transition point is frequently a matter of importance in studies relating to heterogeneous equilibria, since this point defines the limit of stable existence of the two systems. The methods to be described are not applicable to all cases, and the particular method adopted will depend on the nature of the system under investigation.

(1) *Dilatometric Method.*—This method depends on the fact that the greatest change in volume during the heating or cooling of the system occurs at the transition point.

The apparatus employed is a dilatometer (Fig. 37) with a bulb capacity of 30–40 c.c. and a capillary stem about 0·5 mm. in diameter. The substance under investigation is introduced into the bulb together with some of the second modification to induce or facilitate the change at the transition point. The mixture is covered with an air-free liquid in which, for preference, the substance is slightly soluble, so that the transformation may be accelerated. After removing any occluded air-bubbles (with re-course to the pump if necessary), the volume of the liquid is adjusted so that the meniscus is in the lower part of the capillary tube.

FIG. 37. Dilato-meter

The apparatus is placed in a bath which is heated very slowly in order to allow ample time for equilibration. After each degree rise of temperature the height of the meniscus is noted by means of a millimetre scale or a cathetometer. Up to the transition point there will be a regular rise of the liquid on account of ordinary thermal expansion. When the transition point is reached the substance, let us suppose, increases in volume, and this change will be registered by a more rapid upward movement of the meniscus. After the transformation of the first modification into the second form is complete, the liquid will again rise regularly as a result of the normal
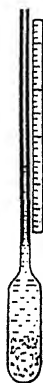
expansion of the system. Similar observations are made while the bath is allowed to cool, and in this case also the maximum volume change occurs at the transition point.

By plotting the height of the liquid against the temperature, as shown in Fig. 38, we obtain the curves $ABCDE$ for rising temperature and $EDFBA$ for falling temperature. Theoretically, the heating and cooling curves should coincide but this is not observed in actual practice owing to molecular hysteresis. However, the transition point may be estimated with fair accuracy by taking the mean value of the temperatures corresponding to the points C and F.

Fig. 38. Volume change at transition point

"*Critical*" *Points of Metals.*—Dilatometric methods find much use in the investigation of transition phenomena of metals and alloys. By the use of appropriate means of amplification, such as mechanical lever transmission or optical magnification, changes in volume at transition or "critical" points may be readily determined. In the Gale dilatometer advantage is taken of the fact that the coefficient of expansion of a metal is much greater than that of silica. A two-inch test-piece of the metal under investigation is placed at the bottom of a closed silica tube and a narrower silica tube placed on top of it as shown in Fig. 39. The upper end of the inner silica tube is attached to a dial gauge, while a thermocouple is placed in the cylindrical hole in the test-piece. When the apparatus is heated in a vertical electric furnace, the movement of the upper end of the test-piece is communicated via the inner silica tube to the dial
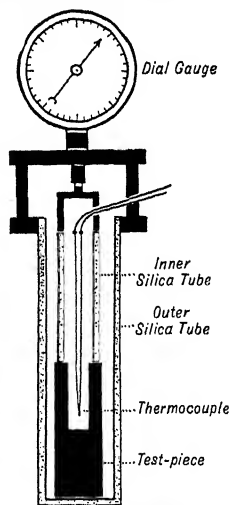
Fig. 39. Gale dilatometer for metals

gauge. The points of anomalous expansion corresponding to phase changes in the metal can be found by plotting the temperature against the change in length as recorded by the gauge.

(2) *Thermometric Method.*—When a pure crystalline solid is heated, its temperature gradually rises until the melting point is reached and the temperature remains constant at this point while the solid is being converted into liquid. Similarly, during the gradual heating of a substance which can undergo transition, the temperature will rise until the transition point is reached and will then remain constant while the transformation of the first system into the second system is taking place. The temperature remains constant owing to the absorption of heat of transformation, and this provides

Fig. 40. Thermometric method

a very convenient and accurate method of determining the transition point.

As applied to sodium sulphate decahydrate the method is briefly as follows. A finely powdered mixture of Glauber's

Fig. 41. Heating and cooling curves

salt and a little anhydrous salt (to induce the change) is placed in a wide test-tube provided with a thermometer and stirrer. The apparatus is supported in a bath or beaker of water with a thermometer and stirrer arranged as shown in Fig. 40. The bath is heated to 28° and maintained at this temperature for half an hour. The temperature of the bath is then slowly raised to 36° at a rate of about 1° in ten minutes. During this process the temperature of the salt is noted every minute, and time-temperature readings are recorded. After passing the transition point, the bath is allowed to cool slowly and time-temperature observations are taken as before. By plotting the temperatures against the corresponding times, we obtain a heating and a cooling curve as shown in Fig. 41, and
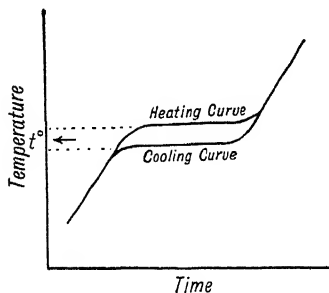
the transition point $t°$ may be readily ascertained from the position of the points of inflexion.

This method was carefully studied by T. W. Richards, who found that the transition points of the following systems are sufficiently definite for use as fixed points in thermometry.

$Na_2SO_4.10H_2O$			soln.	32·383°
$NaBr.2H_2O$	$NaBr$	+	soln.	50·674°
$MnCl_2.4H_2O$	$MnCl_2.2H_2O$	+	soln.	58·089°
$SrBr_2.6H_2O$	$SrBr_2.2H_2O$	+	soln.	88·62°

The direct heating method involving the use of a differential couple for recording the thermal effects may also be employed for determining transition points as described in the case of copper sulphate (p. 71).

The thermometric method can seldom be applied to determine the transition point of simple allotropes, since the change is so slow that the amount of heat evolved in unit time is too small to be measured by an ordinary thermometer.

(3) *Optical Method.*—A substance may change its appearance at the transition point owing to the fact that the frequency of the light absorbed by the first modification is different from that absorbed by the second modification. In this event it is only necessary to ascertain the temperature at which the change in optical appearance sets in.

Mercuric iodide, for example, exists in red and yellow varieties, and the transition point may be determined by observing the temperature at which the crystals change from red to yellow, and vice versa :

$$g$$
red   yellow

Cuprous mercuric iodide Cu_2HgI_4 changes from red to black at the transition point 71°, while silver mercuric iodide changes from a buff colour to yellow at 40°.

Ordinary determinations of the transition point may be carried out by heating the substance in a small capillary tube (Fig. 42 (a)) after the manner of a melting point determination. For more refined work the substance may be placed on an electrically-heated microscope stage (Fig. 42 (b)) and its behaviour examined by an ordinary or polarising microscope.

(4) *X-ray Method.*—The transition from one phase to

another may also be determined by the X-ray method, since different diffraction patterns will be obtained above and below the transition temperature. The recent modifications of the Debye-Scherrer apparatus require the use of only minute quantities of the material and give, moreover, sharp patterns with comparatively short exposures.

(a)   (b)

FIG. 42.   Optical methods

As a result of X-ray studies it is now established that in the transition of certain crystals, such as ammonium nitrate or sodium nitrate, rotation of the molecules or groups may or may not be initiated at the transition point. The definiteness of the transition is referred to the fact that as soon as a molecule changes over from the oscillatory to the rotational state, the neighbouring molecules follow suit and the new molecular

FIG. 43.   Vapour pressure method

forces lead to a new crystal lattice. By taking a series of X-ray pictures at different temperatures, the point at which the lattice goes over to the new lattice can be readily ascertained. The X-ray investigation of the material thus furnishes a powerful method for the study of phase changes in the solid state.

(5) *Vapour Pressure Method.*—The determination of the point at which the vapour pressures of the two systems become equal is carried out in a tensimeter of the type illustrated in Fig. 43. It consists essentially of two bulbs, A and B, in communication with a manometer M, which registers the difference in pressure between the two systems. The first system is placed in A and the second system in B, and after introducing an inert manometric liquid the apparatus is evacuated and sealed. The difference in level of the liquid in the two limbs of the manometer will be a measure of the difference in vapour pressure of the two systems.
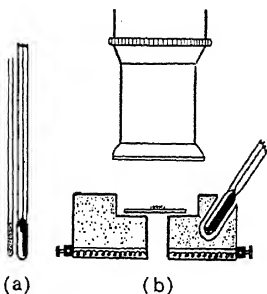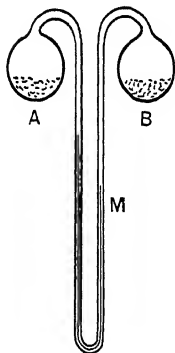
The apparatus is placed in a suitable bath and the temperature gradually raised. As the transition point is approached the difference in height becomes less and less, until it finally becomes zero at the transition temperature. At this point the vapour pressure of the system in A is equal to that of the system in B.

(6) *Solubility Method.*—This method depends on the fact that the two solids have the same solubility at the transition point. The method consists in determining the solubility of each form at a series of temperatures and finding the point of intersection of the two solubility curves thus obtained.

The solubility determinations are carried out according to the usual procedure, care being taken that equilibrium is
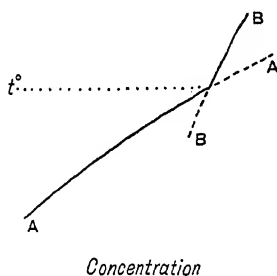
Concentration	*Concentration*
FIG. 44. Solubility of enantio- tropic forms	FIG. 45. Solubility of mono- tropic forms
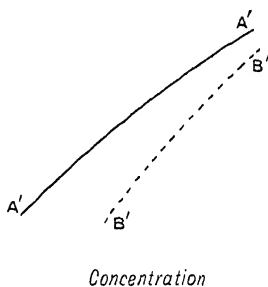
established between the solid phase and the solution by recourse to agitation for a suitable period in a thermostat. A small amount of the saturated solution is withdrawn and weighed, and the quantity of dissolved substance determined by analysis. As a further control, a little of the solid is also removed and analysed in order to ascertain the nature of the solid phase actually in contact with the solution.

Similar measurements are made at a series of different temperatures and the solubility curves are plotted as shown in Fig. 44. The curve AA represents the solubility of the first modification and BB that of the second modification. At the intersection of the two curves the solubilities of the two forms are identical and this is the transition point. The dotted prolongations correspond to metastable conditions, and it is evident that the metastable form always possesses the greater solubility at any given temperature.

The method may also be used in the study of monotropic substances as indicated in Fig. 45. It is often possible to determine the solubility curve $B'B'$ of the metastable form if care is taken to avoid the intrusion of crystals of the stable form. This curve which lies entirely beyond the solubility curve $A'A'$ of the stable form shows that the transition point does not lie within the range of observations.

(7) *Electrical Conductivity Method.* In certain cases where the transformation of one hydrate into the other takes place very slowly, the transition point may be determined by measuring the conductivities of saturated solutions of the two forms over a range of temperatures which includes the transition temperature. Since the two forms have the same solubility and the same conductivity at the transition temperature, the

Conductivity

FIG. 46. Conductivity method

two curves obtained by plotting the conductivity against the temperature will intersect at the transition point as shown in Fig. 46.

This method was successfully employed by Ernst Cohen in the case of the hydrates $ZnSO_4.7H_2O$ and $ZnSO_4.6H_2O$ which undergo transition at 39°.

(8) *Electromotive Force Method.*—This important method may be illustrated by reference to Cohen's determination of the transition point of zinc sulphate heptahydrate.

If the two elements of a cell consist of a zinc rod in zinc sulphate solution, an E.M.F. will be obtained if the solutions have different concentrations. When, therefore, the solutions are saturated with heptahydrate and hexahydrate, respectively, the saturated solutions will have different concentrations at all temperatures other than the transition temperature. Below 39° the hexahydrate being metastable will possess the greater solubility and its saturated solution the greater concentration. Accordingly, a current will flow from the heptahydrate to the hexahydrate. Above 39° the current will be reversed, but at 39°, the E.M.F. being zero, there will be no current in the cell.

The two halves of the cell (Fig. 47) are separated by a stopcock to prevent the mixing of the two solutions. One limb is charged with solid hexahydrate and its saturated solution and the other limb with solid heptahydrate and its saturated solution. The stopcock is opened and the apparatus tilted to remove air-bubbles from the bore of the tap, which is then closed. Zinc rods are immersed in the solutions and connected to a suitable potentiometer. The cell is allowed to stand in a thermostat at 25° and is occasionally shaken to assist the attainment of equilibrium. The stopcock is then opened and the E.M.F. measured in the usual way. The measurement is repeated after 15 minutes to ensure that complete saturation has been attained. The stopcock is closed, the temperature raised by 5°, and the E.M.F. again measured. When the measurements are repeated at intervals up to 50°, it will be found that the E.M.F. falls to zero at 39° and changes its sign above this temperature.
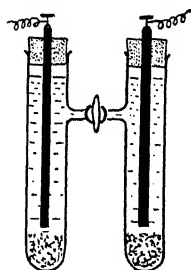
Fig. 47.   E.M.F. method

(9) *Viscosity Method.*—Dunstan and his collaborators have determined the transition points of various salts by measuring the viscosities of saturated solutions at a series of temperatures. By plotting the viscosities against the temperature two curves are obtained which intersect at the transition point. This method has been used to find the transition point of a racemate into a mixture of *d*- and *l*-tartrates.

PRACTICAL METHODS

10. Determination of Transition Points.

i. *Dilatometric Method.*—The bulb *A* (Fig. 48) is charged with a mixture of rhombic and monoclinic sulphur and the tube *B* is fused on to the capillary tube *C*. Dilute sulphuric acid may be used as the dilatometric liquid. The air is pumped off through a suitable adaptor *D* and the liquid is admitted until the apparatus is filled to a convenient point in the capillary.

The dilatometer is provided with a suitable scale *E* and is

then immersed in a bath of strong sulphuric acid. The bath is heated very slowly and the height of the liquid noted for every degree rise of temperature. After passing the transition point the flame is turned down and similar observations are made as the system cools. The expansion (in scale readings) is plotted against the temperature, and the transition point ascertained by taking the mean of the temperatures corresponding to the inflexion points of the heating and cooling curves, as indicated in Fig. 38.

The transition point of ammonium nitrate (32°) may be determined in a similar manner by charging the dilatometer with powdered ammonium nitrate and methylated spirit, and heating the apparatus in a beaker of water.

ii. *Optical Method.*—A little cuprous mercuric iodide is introduced into a capillary melting point tube and fixed to a thermometer as shown in Fig. 42. The thermometer is immersed in a beaker of water and the liquid stirred while the temperature is raised. The temperature at which the substance changes from red to black is noted. The reverse colour change occurs on cooling, but at a lower temperature than the true transition point owing to molecular hysteresis.
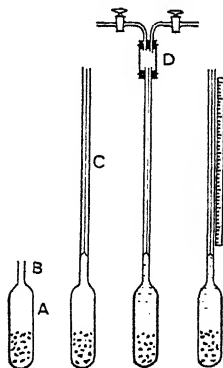
Fig. 48.   Preparation of dilatometer

The transition phenomena of mercuric iodide may be examined in a test-tube containing a coating of the red modification. When the test-tube is heated in a bath of sulphuric acid, the red allotrope is converted into the yellow form at 126°. The yellow mercuric iodide may be cooled to ordinary temperature without changing from its metastable condition, but when touched with a glass rod it reverts immediately to the stable red form.

iii. *Thermometric Method.*—This is by far the best way to determine the transition point of sodium sulphate decahydrate and the experiment is carried out as described on page 89.

iv. *Solubility Method.*—The following precautions must be duly observed in all solubility determinations :

    (*a*) The temperature must be kept constant in a thermostat.
    (*b*) The attainment of true equilibrium between the solid

and the solution is essential. This is ensured in two ways—by thoroughly agitating the mixture for a sufficient length of time or by approaching the equilibrium from both sides.[1]

(c) The solid phase actually in contact with the solution must be analysed in order to ensure that it has not changed into another solid phase at the temperature of the experiment. Thus, if we attempted to determine the solubility of Glauber's salt at 50°, where it would be converted into anhydrous sodium sulphate, the solubility would refer to this solid phase and not to Glauber's salt.

The solubility of the sodium sulphate decahydrate system at various temperatures may be determined in the following
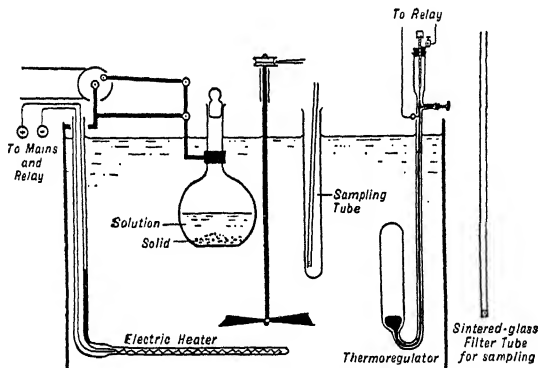
FIG. 49. Measurement of solubility

way. Finely-powdered sodium sulphate crystals and a suitable volume of pure water are introduced into a glass-stoppered flask. The flask is attached to a shaking mechanism (Fig. 49) and the mixture is agitated in the thermostat at the specified constant temperature. After some hours the shaking is stopped and the excess solid allowed to settle to the bottom of the solubility vessel. In order to withdraw some of the solution for analysis, use is made of a glass tube with a small

[1] The equilibrium is said to be approached from both sides when the system is heated to the required temperature and then analysed, and also heated above this point, then allowed to cool to the required temperature, and again analysed.

filter of sintered glass at its lower end. While the solution is coming to equilibrium, this pipette is kept in a glass holder in the same thermostat, so that the solution will not be cooled when the end of the pipette is introduced into the liquid.

Without taking the flask from the thermostat, the stopper is removed and the end of the pipette is carefully lowered into the solution. By applying mouth-suction at the open end, a small amount of the solution is drawn into the pipette. The pipette is withdrawn from the flask and the liquid is run into a previously weighed weighing-bottle. After weighing the solution, it is washed out into a beaker and analysed. In the present case, the sulphate is precipitated by means of barium chloride, and from the weight of barium sulphate produced, the amount of sodium sulphate in the weighed amount of solution may be found. The solubility may be expressed as the number of grams of salt in 100 grams of solution.

The determination is repeated after agitating the solution for a further period in the thermostat, and if the solubility values agree, it is safe to assume that the system has attained equilibrium.

In order to be absolutely certain, however, the equilibrium may be approached from above. For this purpose the flask is removed to another bath at a higher temperature and then returned to the thermostat so that the extra salt dissolved at the higher temperature may settle out. If, after this treatment, the solubility is found to be the same as that given by the first method, it is certain that true equilibrium has been established.

Similar experiments are carried out in thermostats at 25°, 28°, 31°, 34°, 37° and 40°, and the solubility curve plotted in the usual way. It will be found that there are two curves which intersect at the transition point, as indicated on page 92.

These conclusions may be verified by separating some of the solid phase after each solubility determination. By means of a long nickel spatula a small portion of the salt is removed from the flask and quickly dried between filter-papers (no heating being permissible). It is weighed and the amount of Na_2SO_4 present in the solid determined by analysis as before. It will be found that the solid phase below $32 \cdot 4°$ is $Na_2SO_4 . 10H_2O$, while the solid phase in contact with all solutions above this temperature is the anhydrous salt.

QUESTIONS

1. The transition point between anhydrous sodium sulphate and sodium sulphate decahydrate is at 32° C. Describe three experimental methods of determining the transition temperature, explaining the principle involved in each.   (B.Sc., Sheffield.)

2. Explain by means of diagrams and by reference to suitable examples the difference between monotropy and enantiotropy.

Describe in detail one method you would employ to determine the transition point of the system :

$$NaBr.2H_2O \qquad NaBr + Solution.$$
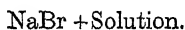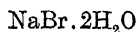
(B.Sc., Wales.)

3. Describe how you would determine the solubility of $MgSO_4.7H_2O$ in water at 40°.

100 parts of water dissolve—

4	parts of A at	0°	44	parts of B at	27·5°
10		10	44·2	,,	,,	30
15·5		15	45·4			32·.
29·5		25	47			35
39		30	54·8			40
50·2		35	66			45
58·5		37·5				

Plot the solubility curves of A and B on as large a scale as possible on the squared paper provided and indicate clearly the portions of the curves which represent the metastable condition. Deduce the transition temperature of $A \rightleftharpoons B$.

Describe in detail one other method for the determination of transition temperatures.   (B.Sc., Manchester.)

4. Give a critical account of the determination of the solubility of a solid in a liquid over a range of temperature. In the case of a dimorphous substance explain how its transition point may be determined by measurements of solubility.

(Sub. B.Sc., Birmingham.)

5. What is a transition point, and how may one be determined experimentally ? Why are true transition points sharp and why do some systems capable of existence in more than one form show no definite transition point ? To what extent are transition points influenced by pressure and by the presence of foreign substances ?   (Final Honours, Oxford.)

CHAPTER V

SOLUTIONS OF LIQUIDS IN LIQUIDS

And sure, the reverent eye must see
A purpose in Liquidity.—RUPERT BROOKE

59. The Behaviour of Liquids.—Some liquids mix with one another in all proportions (e.g. water and alcohol) while other liquids are practically immiscible (e.g. water and mercury). Many cases are known, however, in which the liquids are *partially miscible* with one another. Thus, if we shake together water and ether, some of the ether dissolves in the water and some of the water in the ether, so that two saturated solutions finally separate, as represented in Fig. 50. Two such mutually saturated solutions existing in equilibrium at a particular temperature are termed *conjugate solutions*.

Ethereal Solution of Water

Aqueous Solution of Ether

Miscibility and the Critical Solution Temperature

FIG. 50. Conjugate solutions

We may now consider the miscibility relationships in the three most common types of liquid/liquid systems.

60. Type I. Increasing Mutual Solubility. Upper C.S.T.— The behaviour of these and similar systems may be represented by a *tc*-diagram in which the concentration is expressed as percentage composition or as molar concentration.

Phenol and Water.—When we add phenol to water at ordinary temperature it continues to be dissolved until the concentration of the solution has reached about 8 per cent. The addition of more phenol results in the formation of a second liquid phase, which may be considered to be a solution of water in phenol. If now we raise the temperature, the second

liquid phase will disappear at the *miscibility point*, and more phenol must be added in order to produce two liquid phases. By increasing the amount of phenol in this manner and observing the temperature at which the system becomes homogeneous, the so-called solubility curve of phenol in water may be determined.

The solubility of phenol in water increases with rise of temperature as indicated by the curve AB in Fig. 51. The solubility of water in phenol also increases as we raise the temperature, as represented by the curve CB. The solubility curves approach each other because the compositions of the two conjugate solutions become more nearly the same as the temperature is raised. The two curves do not intersect but meet at a certain temperature, which is called the *critical solution temperature* or consolute point. At this point the two conjugate solutions have attained the same composition ; they have, in fact, become identical and consequently miscible in all proportions.

FIG. 51.   Miscibility of Water and Phenol

In applying the Phase Rule to the system at the critical point we must take into account an extra restriction, viz. that the two liquid phases infinitely near the critical point must be identical (p. 20). This will be equivalent to removing a degree of freedom, so that we may write—

$$P + F = C + 2 - \text{Identity Restriction},$$
$$3 + F = 2 + 2 - 1,$$
$$F = 0.$$

Since the system is invariant at the critical point, the temperature will be a fixed point if the pressure is kept constant

as in ordinary laboratory experiments. Under these condi-
tions, therefore, the critical solution temperature will depend
only on the nature of the two liquids.

For the phenol/water system the critical solution tempera-
ture is 68·3° and the corresponding critical concentration 33·0
per cent of phenol.[1] As indicated in Fig. 51 we can have two
conjugate solutions in heterogeneous equilibrium at any
temperature below the critical solution temperature, but it is
impossible to obtain two liquid layers above this point. If we
prepare a phenol/water mixture of composition and temperature
represented by any point within the area ABC, it will separate
into two liquid phases or binary conjugate solutions. On the
other hand, a mixture of phenol and water of composition and
temperature represented by any point outside the area ABC
will remain as a clear, homogeneous solution.

Incidentally, we have here a good illustration of the
arbitrary manner in which we employ the terms "solvent"
and "solute". Although it is found convenient to make this
discrimination in practice, it should be borne in mind that
there is in the solution itself no actual distinction of this kind.
Indeed, sugar dissolves in water, but it is equally correct to
say that water dissolves in sugar.

Other pairs of liquids which exhibit an upper critical
solution temperature are aniline/water (C.S.T. 167°), acetic
acid/cyclohexane (C.S.T. 4·2°) and methyl alcohol/cyclohexane
(C.S.T. 45·5°). The phenomenon is also observed in some
metallic systems, as for example with bismuth and zinc, which
form two liquid layers with a critical solution temperature
at 850°.

61. Type II. Decreasing Mutual Solubility. Lower C.S.T.—
Several cases are known in which the solubility of one liquid
in another decreases as the temperature is raised.

Triethylamine and Water.—Triethylamine $(C_2H_5)_3N$ and
water mix together in all proportions below 19°, but on raising
the temperature the homogeneous solution becomes turbid and
separates into two layers. The behaviour of the system with
respect to temperature and concentration is shown in Fig. 52.
The curve AB shows the decreasing solubility of triethylamine
in water ; the curve CB the decreasing solubility of water in

[1] According to the most recent investigations the C.S.T. of highly
purified phenol is 66·5°. It is interesting to note that the C.S.T. for
the phenol/deuterium oxide system is 78·2°.

triethylamine.   The two curves meet at B, which is thus a lower critical solution temperature.

Other pairs of liquids which behave similarly are dimethyl-amine/water and paraldehyde/water.   These liquids are more soluble in one another at low temperatures than at high, and the curves show therefore a minimum temperature of complete miscibility.

With respect to the behaviour of ether and water it is interesting to note that the solubility of water in ether increases while the solubility of ether in water decreases with rise of temperature, so that the case is rather different from either of the above systems.
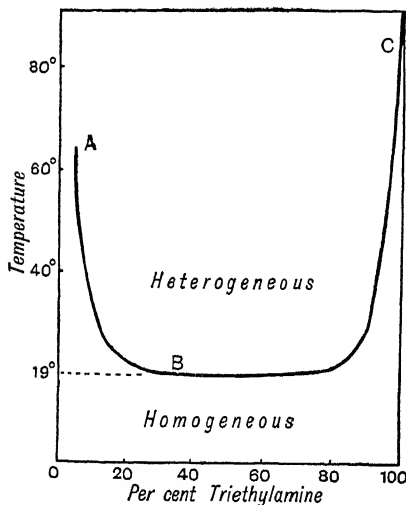
FIG. 52.   Miscibility of Water and Triethylamine

62. **Type III.   Closed Solubility Curve.   Upper and Lower C.S.T.**—In a few cases it is found that the mutual solubility curve is a closed curve with an upper and a lower critical solution temperature.

Nicotine and Water.—The miscibility relationships of nicotine ($C_{10}H_{14}N_2$) and water are represented in Fig. 53.   At temperatures below 61° and above 208° the two liquids are completely miscible.   Between 61° and 208° they are only partially miscible.   Accordingly, the mutual solubility curve is a closed one with an upper critical solution temperature at 208° and a lower critical solution temperature at 61°.

In connexion with the mutual solubility curve in all three types of system, it should be noted that it is *continuous.* Clearly, breaks in the curve could occur only if some discontinuity arose in one of the phases, i.e. if the character of the phase changed.   The mutual solubility curve should not be regarded as comprising two solubility curves intersecting at a point, because, actually, it is a curve of equilibrium

between two phases which are undergoing continuous change. The critical solution temperature represents, therefore, not the intersection, but rather the *point of merging* of the two curves.

63. The Influence of Impurities. The Crismer Test.—For a given pressure the critical solution temperature is a perfectly defined point, but it is very sensitive to the presence of impurities. It is, in fact, much more sensitive to impurities than other physical properties such as density, refractive index, melting point or boiling point. The determination of the critical solution temperature may therefore be used for testing the purity of liquids.

Crismer was the first to demonstrate this extreme sensitiveness of the critical solution temperature to dissolved impurity. He found that the critical solution temperature of ethyl alcohol and petroleum was raised to the extent of 17° by the presence of merely 1 per cent of water in the alcohol. Methyl alcohol and cyclohexane have a critical solution temperature at 45·5°,

FIG. 53.   Miscibility of Water and Nicotine

and even such a small amount as 0·01 per cent of water in the methanol produces an easily measurable rise of 0·15° in the critical solution temperature.[1]

Pure glacial acetic acid and cyclohexane have a critical solution temperature at 4·2°, as shown in curve I (Fig. 54), where K_1 is the critical temperature. The addition of merely 0·2 per cent of water to the acid changes the form of the mutual solubility curve to that of curve II, with the critical solution temperature K_2 about 4° higher than K_1. The system is now a three-component system since it consists of acetic acid, cyclohexane and the impurity, water. The

[1] D. C. Jones, *J. Chem. Soc.*, 1923, 1374.

presence of 1 per cent of water causes a still greater change in the mutual solubility curve and the critical solution temperature K_3 is 18° above that found for the anhydrous binary system. The determination of the critical solution temperature thus affords an excellent method of detecting traces of water in glacial acetic acid. In a similar manner the amount of deuterium oxide in D_2O/H_2O mixtures can be estimated by determining the critical solution temperature with phenol.

Petrol and aniline have an upper critical solution temperature which is sensitive to the presence of impurities in the petrol. By determining the critical solution temperature of a given petrol with aniline it is possible to detect and estimate the amount of aromatic hydrocarbons present in the petrol. Similar methods have been applied to determine the amount of ceresin in wax.
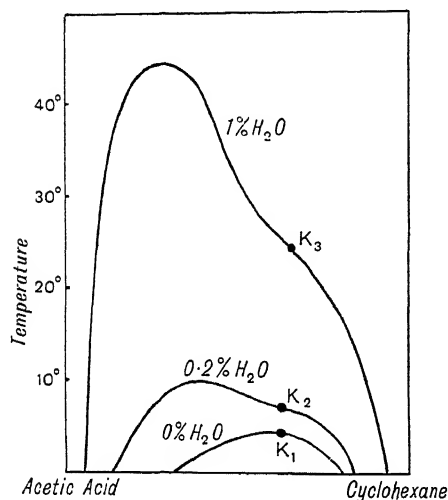
FIG. 54.   Effect of impurity on C.S.T.

Urine has also been tested for dissolved matter by finding its critical solution temperature with phenol. A kidney producing urine which gives a critical solution temperature rise of 8° is in good order, and is functioning exceedingly well if the rise is 11–16°.

In general, the critical solution temperature is raised if the third substance is soluble in one of the liquids only, and lowered if it is soluble in both liquids. Advantage is taken of the latter effect in the commercial preparation of the well-known disinfectant " Lysol ". The cresols and water do not mix completely, but the addition of a small amount of soap lowers the miscibility temperature so that " Lysol " exists as a clear liquid at ordinary temperature, and there is no need to shake the bottle before use.

PRACTICAL METHODS

11. **Determination of the Critical Solution Temperature.**—
A test-tube, constricted to the shape shown in Fig. 55, is
thoroughly cleaned, dried and weighed. The tube is charged
with about 1 gram of pure dry phenol and accurately re-
weighed. After introducing about 4 c.c. of water the tube is
weighed again and then sealed at the constriction. Further
tubes containing 1·5 g. phenol : 3·5 g. water, 2 g. phenol : 3 g.
water, 2·5 g. phenol : 2·5 g. water and 3 g. phenol : 2 g. water
are prepared in a similar manner. The miscibility temperature
for each system is then determined according
to the following procedure.

The tube is held in a stout wire holder
and immersed in a large beaker of water
whose temperature is registered by an accu-
rate thermometer. The bath is heated while
the submerged tube is vigorously shaken,
and the temperature at which the turbid
liquid suddenly becomes clear is noted. The
bath is allowed to cool and the temper-
ature again noted when the liquid becomes
turbid.[1] These operations are repeated until
close agreement between the two temper-
atures is obtained. The mean of these
readings gives the temperature at which
1 gram of phenol is completely soluble in 4 grams of water.

Fig. 55. Deter-
mination of
miscibility
point

The miscibility temperatures for the other systems are
determined in the same way, and the critical solution tempera-
ture is ascertained from the smooth curve obtained by plotting
the miscibility temperatures against the percentage composition
of phenol in the mixtures.

12. **To Examine the Effect of Impurity on the C.S.T.**—The
critical solution temperature of a specimen of pure phenol
and pure water is determined as described above. A small
quantity of urea (equivalent to 1 per cent) is added to the
water and the critical solution temperature again determined.
From the displacement of the critical solution temperature
it is possible to estimate the minimum amount of urea which
can be detected with the equipment used.

[1] Einstein (*Ann. Physik.*, 1910, **33**, 1275) has developed an interesting
theory concerning the turbidity in the neighbourhood of the critical point.

The same procedure may be applied to estimate traces of water in methyl alcohol by determining its critical solution temperature with pure cyclohexane.

QUESTIONS

1. What is meant by the terms, *component, phase, degree of freedom* ? How many degrees of freedom are possessed by the systems :

(a) $CaCO_3 \; \overset{\longleftarrow}{\longrightarrow} \; CaO + CO_2$;

(b) gaseous $NH_4Cl \; \overset{\longrightarrow}{\longleftarrow} \; NH_3 + HCl$;
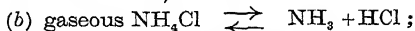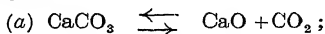
(c) phenol and water below the critical solution temperature ?
(B.Sc., Reading.)

2. State the Phase Rule, defining the terms used. Discuss from the point of view of the rule, and by reference to diagrams, the solutions formed by two liquids which are only partially miscible at room temperature.   (B.Sc., London.)

3. Give an account of the Phase Rule relations of the two-component system formed by water and a substance such as phenol, which melts at about 40° and possesses a critical solution temperature in the liquid state.   (Final Honours, Oxford.)

4. What are the possible forms of solubility curves for pairs of partially soluble liquids ? Describe how you would obtain the curve for the system phenol-water.   (B.Sc., Sheffield.)

5. Compare and contrast (a) a " gas-liquid " system near its critical temperature and (b) a " liquid-liquid " system near its critical solution temperature.   (Sub. B.Sc., Birmingham.)

6. How would you proceed to determine the critical solution temperature of phenol and water ?   Give an example of the utility of this property as a criterion of liquid purity.   (B.Sc., Wales.)

THE VAPOUR PRESSURE AND DISTILLATION OF LIQUID MIXTURES

Fanning their odoriferous wings, dispense
Their perfumes and whisper whence they stole
Those balmy spoils.—MILTON

64. **Classification of Systems.**—Liquid mixtures may be divided into three classes according to their miscibility, viz. completely miscible, partially miscible and immiscible. The first class may be further divided into three types according as the vapour pressure-composition curve shows neither maximum nor minimum, shows a minimum or shows a maximum. For reasons which will become apparent later, the first type represents zeotropic mixtures, while the second and third types include azeotropic mixtures of maximum or minimum boiling point. It will be convenient therefore to adopt the following general classification :

CLASS I.   COMPLETELY MISCIBLE LIQUIDS

Type I.   Zeotropic Mixtures.
Type II.   Azeotropic Mixtures: Maximum Boiling Point.
Type III.   Azeotropic Mixtures: Minimum Boiling Point.

CLASS II.   PARTIALLY MISCIBLE LIQUIDS
CLASS III.   IMMISCIBLE LIQUIDS

The vapour pressure relationships in the various types of systems may now be discussed with particular reference to the behaviour of the liquids on distillation.

I. COMPLETELY MISCIBLE LIQUIDS

65. **Type I.   Zeotropic Mixtures.**—Zeotropic mixtures are those which do not show a maximum or a minimum on the vapour pressure-composition curve.

Ideal Liquids.—Let us first consider the behaviour of an ideal mixture of two liquids in which the partial pressure of each component is proportional to its molar concentration in the mixture (Raoult's law). In Fig. 56 the partial pressure of component A is represented by the dotted line P_AB falling from its highest value at P_A to the zero value at B when none is present in the mixture. Similarly, the dotted line AP_B represents the partial vapour pressure of the component B. The vapour pressure of a mixture of composition m will consist of a pressure mo due to component A and a pressure mn due to component B. Since op is equal to mn, the actual vapour pressure of the mixture will be given by mp. The total vapour pressure of the mixture is equal to the sum of the partial pressures and is therefore represented by a point on the vapour pressure curve P_AP_B. That P_AP_B is a straight line may be proved by geometry or by construction.

FIG. 56.   Vapour pressure of ideal mixture

Ordinary Liquids.—Mixtures of ordinary liquids, however, do not accurately obey Raoult's law and the actual vapour pressure curve is not a straight line, but a line curving progressively from P_A to P_B. A simple case is shown in Fig. 57 which is a pc-diagram for ordinary mixtures showing no maximum or minimum vapour pressure. In this diagram the point A represents the vapour pressure of component A and the point B that of component B. The upper curve represents the composition of the liquid phase, while the lower curve gives the composition of the vapour phase. If we draw a horizontal line vl to indicate equality of pressure, it is evident that a liquid mixture of composition l is in equilibrium with a vapour mixture of composition v.

For the purpose of discussing the distillation of binary mixtures it is perhaps more convenient to make use of the boiling point-composition diagram shown in Fig. 58, which is

sometimes called the boiling point diagram. This is a *tc*-diagram and its relation to the *pc*-diagram (Fig 57) should be carefully noted. Component *A* with its high vapour pressure will have a low boiling point, component *B* with its low vapour
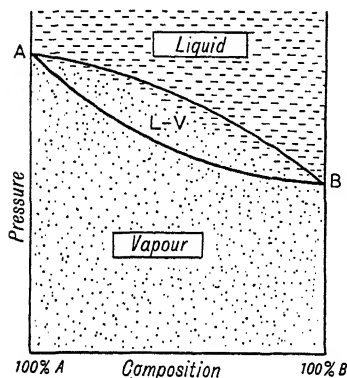
FIG. 57. Vapour pressure diagram of zeotropic mixture
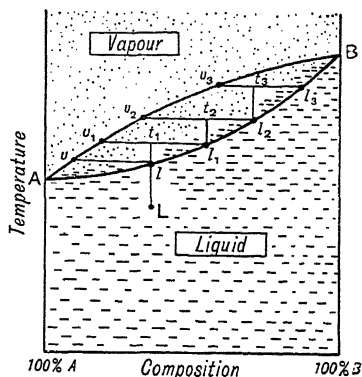
FIG. 58. Boiling point diagram of zeotropic mixture

pressure will have a high boiling point, while similar inverse relationships will hold in the case of corresponding mixtures. In Fig. 58 the upper curve represents the composition of the vapour and may be called the *vaporus*,[1] while the lower curve gives the composition of the liquid, and as such may be termed a *liquidus*.

The *boiling point of a liquid mixture* is the temperature at which the total vapour pressure becomes equal to the external pressure. The determination of the normal boiling point is usually carried out under atmospheric pressure and the term "boiling point" thus signifies the temperature at which the total vapour pressure is 760 mm.

66. **Theory of Fractional Distillation.**—We may use the boiling point diagram to illustrate what happens during the ordinary distillation of a liquid mixture. Suppose we have a

[1] There appears to be no reason why this name should not be given to the vapour composition curve of the boiling point diagram. It is convenient, and also serves to indicate in a sense the analogy with the liquidus and solidus curves of solid/liquid systems described in Chapter VII. It is therefore preferable to the more precise Latin designation *vaporalis*.

liquid mixture of composition and temperature represented by the point L (Fig. 58). As we apply heat, the system remains liquid until the temperature reaches that of l, where, of course, vapour of composition v is formed. If the first removal of vapour from the distillation vessel occurs when the temperature has been raised a little higher to t_1, vapour of composition v_1 condenses in the receiver and a liquid of composition l_1 remains in the distillation flask. When the temperature of the liquid in the flask is raised still further to the point t_2, vapour of composition v_2 is carried over to the receiver and a liquid of composition l_2 remains as residue. Further raising of the temperature to t_3 will produce a vapour of composition v_3 and leave a liquid of composition l_3, and so on. It is evident, therefore, that the composition of the vapour coming over and that of the liquid left behind change continuously as the distillation proceeds, while the boiling point rises throughout. This is predicted by the Phase Rule :

$$P + F = C + 2,$$
$$2 + F = 2 + 2,$$
$$F = 2,$$

so that if the pressure is kept constant the temperature will change as the composition changes.

Consider for example the behaviour of a mixture of benzene (b.p. 80°) and toluene (b.p. 110°). When the mixture is heated the vapour given off consists of benzene and toluene, and the mixture boils when the temperature is such that the sum of the two partial pressures is equal to atmospheric pressure. The constituent of higher vapour pressure (lower boiling point) passes over in greater quantity. As the distillation proceeds, the composition of the residual mixture gradually changes. So also does the temperature which is necessary to preserve the condition that the sum of the partial pressures shall equal atmospheric pressure. As a result of this process the benzene tends to concentrate in the distillate and the toluene in the residue. If the mixture be subjected to fractional distillation through a suitable column a sufficient number of times, practically complete separation of the two constituents can be effected.

It is important to note in this connexion that *the process of fractional distillation can be used only in those cases where the vapour pressure of the mixture changes progressively from that*

of one component to that of the other component. In other words, the method can only be applied to zeotropic mixtures which do not show a maximum or a minimum on the vapour pressure-composition curve.

Fortunately, liquid air is a mixture of this type and it is possible to separate it by fractional distillation into pure nitrogen (b.p. 77° T) and pure oxygen (b.p. 90° T). Liquid argon and liquid neon furnish a similar system which is fractionated on the commercial scale to produce the gases for " neon signs ".

67. Method of Fractional Distillation.—Fractional distillation is the process whereby a mixture of liquids is distilled through a special fractionating column in order to increase the efficiency of the separation. By partially condensing the rising vapours the fractionating column holds back the less volatile liquid and allows the more volatile portion to escape into the condenser and receiver. The ideal column should bring the upward-flowing vapour and the downward-flowing liquid into intimate contact, so that equilibrium is established between the vapour and the liquid at all points. The vapour passing upwards becomes richer and the liquid passing downwards becomes poorer in the more volatile constituent.

We may illustrate the essentials of the method by describing the ordinary laboratory fractionation of a mixture of 50 c.c. of benzene (b.p. 81°) and 50 c.c. of xylene (b.p. 140°). The apparatus, assembled as shown in Fig. 59, consists of a round-bottom flask, a " pear column ", a condenser and adaptor, and a number of receivers. After placing the mixture in the flask (together with a few pieces of porous porcelain to promote even ebullition) [1] the liquid is distilled through the column, so that about two drops of liquid fall from the end of the condenser per second. Actually, it is found that the liquid begins to distil at 87° and that the temperature recorded by the thermometer rises gradually during the distillation. Accordingly, without removing the flame or interrupting the distillation

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[1] When a liquid is heated in a smooth glass vessel the lower layers of the liquid may become *superheated* and may suddenly change into vapour with explosive violence. This phenomenon, which is known as " bumping ", can be prevented by introducing small pieces of porous pot or " boiling stone ". The capillary pores of the porcelain become filled with vapour and the presence of the vapour phase in contact with the liquid thus prevents superheating.

in any way, " fractions " or " cuts " are taken by changing the receiver between predetermined temperature ranges.   The volumes of the various fractions collected in this way are found to differ as indicated in the following table :

Fraction	A	B	C	D	E	Residue
B.P. .	87-100°	100-110°	110-120°	120-130°	130-140°	Above 140°
Volume .	33 c.c.	16 c.c.	8 c.c.	8 c.c.	33 c.c.	2 c.c.

The essential feature of the method is that the fractions are taken according to the boiling point range and not according to the volume of the distillate.

The fraction A is now refractionated and it is found that the largest fraction of the new series is that boiling between

Dufton Column
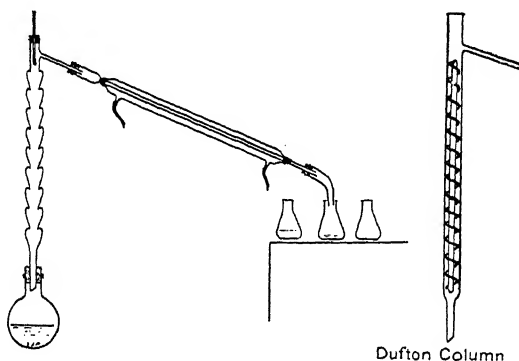
Fig. 59.   Fractional distillation

81-85°.   The other fractions of this series are added to the appropriate fractions B, C or D of the original series.   The fraction E is also refractionated and the largest fraction of this series boils between 135-140°.   As before, the other fractions of this series are added to the appropriate fractions B, C or D.   The process is then repeated separately with B, C and D until the original mixture is ultimately separated into two principal fractions consisting of crude benzene and crude xylene.   With the ordinary pear column the fractionation must be repeated several times in order to obtain the pure constituents.

The Dufton Column.—Fractional distillation is usually a tedious process, and literally hundreds of different types of columns have been designed for the purpose of increasing the

efficiency of the separation. The most common laboratory types are the pear column, the *Hempel* column (filled with glass beads) and the *Vigreaux* column (with indentations along the tube), but these are sadly lacking in efficiency. The most efficient apparatus is the *Dufton* column,[1] which is made by winding copper wire spirally on a rod and fixing the arrangement inside a long glass tube as shown in Fig. 59. The copper spiral fits tightly between the inner and outer tubes so that the ascending vapours and descending liquid pass one over the other in a spiral track extending from the bottom to the top of the column. Such an arrangement is very efficient in establishing equilibrium conditions between the liquid and the vapour, but " piling up " of liquid in the column must be avoided. One distillation through a vacuum-jacketed Dufton column will separate the three constituents from a mixture of benzene, toluene and xylene, and this method is actually used for the commercial analysis of these mixtures.

FIG. 60.   Bell and plate column

68. **Industrial Fractionation.**—The large-scale fractionation of liquid mixtures involves the use of special fractionating columns which permit the separation of the constituents either in one distillation, or continuously as the mixture is fed into the distillation vessel. In all cases, however, the column is designed so that there is a counter-current flow of liquid and vapour.

A sectional diagram of a commercial fractionating column is shown in Fig. 60. The plates and bells are arranged in series so that the liquid and vapour are brought into intimate contact on each plate. The mixed vapours from the distillation vessel enter compartment I, where they are partially condensed, while the more volatile portions pass on to compartment II, and so on. Since the vapours from a lower chamber are hot enough to cause boiling of the liquid in the next upper chamber, the more volatile portions pass on, while the higher boiling material condenses out. As a result of this process the lower boiling material may be led off from the top of the

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[1] *J. Soc. Chem. Ind.*, 1919, **38**, 45T ; 1935, **54**, 297T.

column and the higher boiling constituents withdrawn from the bottom of the column.

Fractional Condensation.—The fractionation process discussed above really consists of the two separate processes of fractional distillation and fractional condensation taking place simultaneously. But it is possible to employ fractional condensation alone, the whole mixture being converted into vapour and then condensed in fractions.

This method, which is largely used in petroleum refineries, is illustrated diagrammatically in Fig. 61. The crude oil from the oil-fields is pumped into a " pipe-still ", where it is heated under pressure. Leaving the " pipe-still ", the liquid passes through a valve into a region of lower pressure and is thus " flashed ", or completely vaporised. The mixed vapours enter the fractionating column and undergo a process of fractional condensation with the result that the constituents are distributed along the column according to their boiling points. The more volatile petrol vapours are not condensed in the column and are led from the top into a separate pipe condenser, but the less volatile paraffins, Diesel oil and lubricating oil are withdrawn by pipes suitably placed along the column. The various fractions are further refined by chemical treatment before they are ready for the market.

Fig. 61.   Fractionation of Crude Oil

69. Type II. Azeotropic Mixtures: Maximum Boiling Point. —An *azeotropic mixture* [1] is one which possesses a lower vapour pressure or a higher vapour pressure than any other mixture. Consequently the mixture may have a boiling point higher or a boiling point lower than any other mixture. Such mixtures separate on distillation, not into the two components, but into one of the components and a constant boiling or azeotropic

[1] Wade and Merriman introduced the term azeotropic in 1911 : " It is proposed, in order to avoid the cumbrous periphrase ' mixtures of minimum or maximum boiling point ', to designate them as azeotropic (from the Greek, meaning *privative, to boil*)."

mixture of both. The *constant boiling mixture* distils unchanged at constant temperature and the composition of the distillate is the same as that of the residual mixture.

Mixtures belonging to Type II are characterised by the fact that the vapour pressure of the constant boiling mixture is lower than that of its constituents, as indicated in Fig. 62. It follows, therefore, that the boiling point of this mixture is higher than that of the constituents or of any other mixture, as shown in the boiling point-composition diagram (Fig. 63).

This behaviour is exhibited by mixtures of water (b.p. 100°) and formic acid (b.p. 99.9°). The vapour pressure-composition
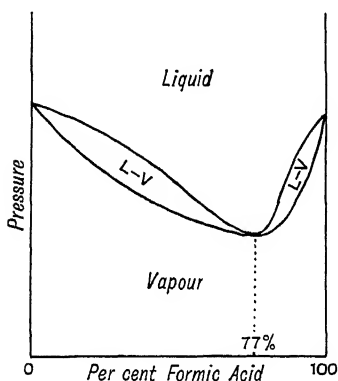
FIG. 62. Vapour Pressure diagram showing azeotropic mixture of minimum vapour pressure
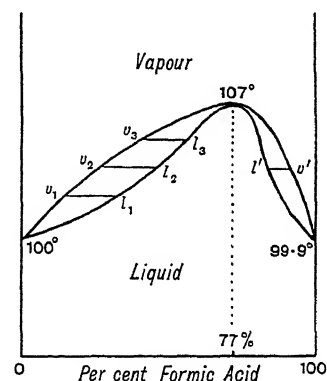
FIG. 63. Boiling point diagram showing azeotropic mixture of maximum boiling point

curve for this system shows a minimum at 77 per cent formic acid (Fig. 62), and this is therefore the *mixture of maximum boiling point* (Fig. 63). When we distil a liquid of composition l_1 (containing less than 77 per cent of formic acid) the vapour will have the composition v_1, which is lower in formic acid than the residue in the distillation flask. In other words, the distillate will be richer in water than the residue. As the distillation proceeds, the temperature will rise while the successive compositions of the residue l_2, l_3, etc. change along the liquidus and those of the vapour v_2, v_3, etc. move along the vaporus. Finally, the composition of the vapour will become the same as that of the residue. This corresponds to the meeting of vaporus and liquidus, and when this point is

reached the residue distils at 107° as a constant boiling mixture containing 77 per cent of formic acid.

When a mixture of composition l' (containing more than 77 per cent of formic acid) is distilled, the vapour will have the composition v', which is higher in formic acid than the residue. Distillation will proceed with rise of temperature while the compositions of vapour and residue move along the vaporus and liquidus, respectively. When the residue and distillate attain the composition of 77 per cent formic acid, the liquid boils at constant temperature (107°) without change in composition. In order to prepare the more concentrated or anhydrous formic acid it is necessary to break up the azeotrope by converting the acid into the insoluble lead formate from which the anhydrous acid may be liberated by the action of hydrogen sulphide.

Mixtures of strong acids with water generally behave in this way and show a maximum boiling point. This behaviour is probably due to the fact that the respective molecules have a great affinity for one another and thus give rise to mixtures of low vapour pressure. Over a thousand azeotropic mixtures of this kind are now known [1] and a few of the more familiar examples are given in the following table :

MIXTURES OF MAXIMUM BOILING POINT

Component A		Component B		Composition		Maximum B.P.
Water	100°	HF	19·5°	37%	HF	120°
Water	100°	HCl	− 80°	20·22%	HCl	108·6°
Water	100°	HBr	− 73°	47·63%	HBr	124·3°
Water	100°	HI	− 35°	58%	HI	127°
Water	100°	H_2SO_4	..	98·7%	H_2SO_4	338°
Water	100°	HCOOH	99·9°	77%	HCOOH	107°
Acetone	56·6°	$CHCl_3$	61·2°	80%	$CHCl_3$	64·7°

The fact that concentrated hydrochloric acid becomes weaker and the dilute acid stronger on boiling was known to Dalton as long ago as 1802. The simple boiling point diagram for aqueous solutions of hydrochloric acid reveals a maximum at a concentration of 20·22 per cent hydrochloric acid (Fig. 64). Advantage is taken of this azeotropic behaviour in the preparation of standard solutions for analytical purposes. If a

[1] Lecat, *L'Azeotropisme*, Bruxelles, 1918.

hydrochloric acid solution of any concentration be taken and boiled in the open air (760 mm. pressure) for a sufficient length of time it will attain the exact composition 20·22 per cent HCl. This standard solution may then be diluted to any desired strength (p. 139).

70. **Type III. Azeotropic Mixtures : Minimum Boiling Point.**—The vapour pressure-composition curves of these mixtures exhibit a maximum, while the corresponding boiling point curves show a minimum as represented in Figs. 65 and 66. Such a mixture may be separated into one of

FIG. 64. Boiling point-composition curve for HCl solutions

the components and the *mixture of minimum boiling point*, but it is impossible to fractionate the mixture into the two separate components.

n-Propyl alcohol (b.p. 97·2°) and water mix together in all proportions, and of all the possible mixtures the one containing
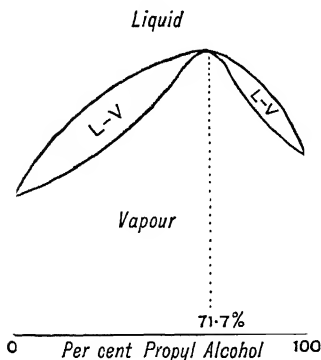
'IG. 65. Vapour pressure diagram showing azeotropic mixture of maximum vapour pressure
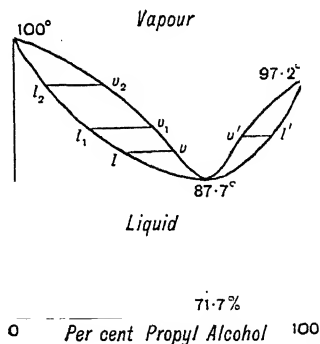
FIG. 66. Boiling point diagram showing azeotropic mixture of minimum boiling point

71·7 per cent of propyl alcohol possesses the highest vapour pressure (Fig. 65). It is therefore the mixture of minimum boiling point (Fig. 66). If we heat a solution of composition

corresponding to l_1 the vapour or distillate will have the composition v_1, and, as distillation proceeds, the composition of the residue will change to l_2 and that of the vapour to v_2. Accordingly, the residue will contain more water than originally, while the combined distillates will have a composition intermediate between v_1 and v_2. Let the actual composition of the distillate be represented by the point l. If, now, we distil this liquid, the vapour will have composition v, which is still nearer to the composition of the azeotrope. In fact, by repeating the separate distillation of the original residue and the original distillate we can separate the given liquid mixture into pure water and the azeotrope. Similarly, if the given mixture has the composition l' it can be resolved into pure propyl alcohol and the azeotrope.

Ordinary ethyl alcohol and water behave in the same way and give rise to an azeotrope containing 96 per cent of alcohol and boiling 0·15° lower than pure ethyl alcohol. Accordingly, it is impossible to concentrate alcohol beyond this strength by distillation alone.

<div align="center">MIXTURES OF MINIMUM BOILING POINT</div>

Component A	Component B	Composition	Minimum B.P.
Water 100°	Ethyl alcohol 78·3°	96% C_2H_5OH	78·15°
Water 100°	Propyl alcohol 97·2°	71·7% C_3H_7OH	87·7°
Water 100°	Butyric acid 159°	20% $C_4H_8O_2$	99·2°
Water 100°	Pyridine 115°	59% C_5H_5N	92°
Benzene 80·2°	Ethyl alcohol 78·3°	32·4% C_2H_5OH	68·2°
Acetone 56·6°	Methyl alcohol 65·5°	13·5% CH_3OH	56°

Owing to the existence of azeotropism the preparation of absolute ethyl alcohol by the fractionation of the simple alcohol/water mixture is impossible, and it is necessary to remove the water by means of lime before the anhydrous liquid can be obtained. Methyl alcohol, however, does not form an azeotropic mixture with water.

71. **General Characteristics of Azeotropism.**—An azeotropic mixture may be defined as *a mixture which possesses either* (a) *a higher vapour pressure or* (b) *a lower vapour pressure than any other mixture of the components.* According to a rule deduced by Willard Gibbs, *the vapour pressure attains a maximum or a minimum when the liquid and vapour phases attain the same*

composition. It is clear from Figs. 62 and 65 that the liquid and vapour phases are identical when the liquidus curve meets the vaporus curve.

The Phase Rule predicts that an azeotrope will boil at constant temperature, but in this case we must introduce an identity restriction since the vapour and liquid phases have identical composition. Accordingly, we have

$$P + F = C + 2 - \text{Identity Restriction},$$
$$2 + F = 2 + 2 - 1,$$
$$\text{and} \qquad F = 1,$$

so that the boiling point will be constant if the pressure is fixed. It offers no information, however, as to whether the mixture will be a maximum or minimum boiling mixture.

Since the constant boiling mixture distils unchanged, it cannot be resolved into its components by the application of any process of fractional distillation. In fact, the process of fractional distillation can be used only for the separation of zeotropic mixtures, whose vapour pressures lie on a continuous curve with no maximum or minimum.

The behaviour of a constant boiling mixture on distillation simulates that of a pure compound, because the composition of the vapour phase is the same as that of the liquid phase. This mixture, however, cannot be regarded as a true chemical compound, since the composition is not constant under all conditions. Actually, the composition of the constant boiling mixture depends upon the pressure at which the distillation is conducted. Moreover, the composition of the azeotrope rarely corresponds to stoichiometric proportions, and the Raman spectrum gives no indication of compound formation.

The Breaking Up of Azeotropic Mixtures.—In many industries the breaking up or resolution of a constant boiling mixture is a matter of great importance and a variety of methods are used in practice according to the nature of the constituents. In principle, of course, an azeotropic mixture might be broken up by alternate distillations under radically different pressures, but this method would be extremely tedious owing to the small changes in composition involved. An azeotropic mixture, however, may be broken up by one of the following methods.

(1) Distillation with a third substance which alters the vapour pressure ratios in the azeotrope. This method has

been successfully employed in the isolation of hydrocarbons by distilling with alcohol, and in the preparation of absolute alcohol by distilling with benzene (p. 251).

(2) Fractional extraction may be used in some cases, since the constituents distribute themselves in a new proportion in the solvent. Liquid sulphur dioxide and aniline have been used for separating petroleum mixtures in this way.

(3) Fractional crystallisation may be carried out directly on the liquid mixture or after dissolving it in a suitable solvent. The customary procedure consists in freezing the entire azeotrope and then allowing it to melt slowly in a centrifuge so that the successive liquid fractions are removed as they are produced. The various melts are returned to the still and separately fractionated by further distillation. By alternating fractional crystallisation with fractional distillation, most azeotropic mixtures can be resolved into their components.

(4) Chemical methods may be used to break up an azeotrope if the reagent attacks one of the components only. Thus lime is employed for removing water in the preparation of absolute alcohol, and lead carbonate in the preparation of anhydrous formic acid. In the case of mixtures containing aromatic hydrocarbons one component can frequently be removed by nitration or sulphonation.

(5) Preferential adsorption of one of the components may also be used for the same purpose. Silica gel or charcoal may be used in this way to adsorb one of the components of the azeotrope in preference to the other. If the adsorbate is easily recoverable, the process may be adapted for the complete separation of the azeotrope into its components.

Uses of Azeotropism.—The phenomenon of azeotropism is taken advantage of both in the laboratory and in nature. Among these processes we have

(a) the preparation of standard solutions, such as hydro-
    chloric acid ;
(b) the purification of substances, such as the preparation
    of absolute alcohol through the azeotropic elimination
    of water by distillation with benzene ;
(c) the estimation of moisture in powders by azeotropic
    distillation of the water with organic liquids ;
(d) the evaporation of perspiration from the skin.

In connexion with the last process it may be recalled that the pores of the skin exude a ceaseless stream of perspiration con-

sisting of 99 per cent of water and 1 per cent of fatty acid. The fatty acid is removed from the surface of the skin by azeotropic evaporation, since the boiling point of the mixture is much lower than that of the constituents.

II. PARTIALLY MISCIBLE LIQUIDS

72. **Vapour Pressure and Distillation Phenomena.**—If two liquids are partially miscible the vapour pressure of the two conjugate solutions is always less than the sum of the vapour
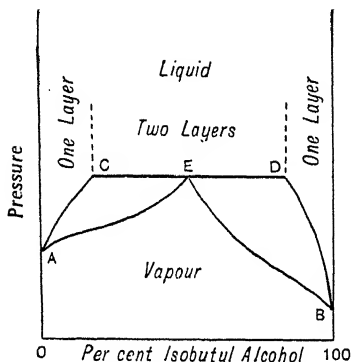
FIG. 67.   Vapour pressure diagram of partially miscible liquids
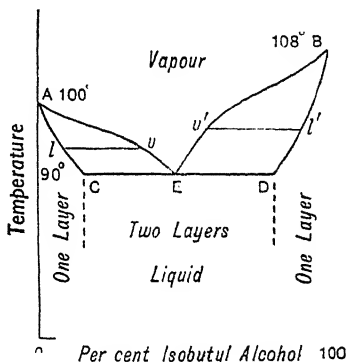
FIG. 68.   Boiling point diagram of partially miscible liquids

pressures of the pure components since each liquid depresses the vapour pressure of the other.

This behaviour is exemplified by isobutyl alcohol and water mixtures which have the vapour pressure-composition curves shown in Fig. 67. If we add isobutyl alcohol to water the vapour pressure increases along the upper curve AC until a saturated solution is obtained. This is to be anticipated on the premises of the Phase Rule, inasmuch as the system contains one liquid phase and one vapour phase, and is therefore bivariant. At C, however, two liquid layers are present, and since the total number of phases is now three the system is univariant. Accordingly, if we fix the pressure, the temperature of distillation and the composition of both vapour phase and distillate will be fixed.

As indicated in the corresponding boiling point diagram (Fig. 68) the mixture will distil at a constant temperature so long as two liquid phases are present. The only result of

distillation will be to change the relative quantities of the two layers, and the boiling point will remain constant until one of the layers disappears. When this occurs the system once more assumes the bivariant state, and the boiling point will then change with composition in normal fashion until it attains the value for one of the pure components. Konowaloff found that the boiling point of the two-layer system is 90° while that of pure isobutyl alcohol is 108°.

If we distil a two-layer system of composition between C and D, the boiling point will be 90° and the distillate will
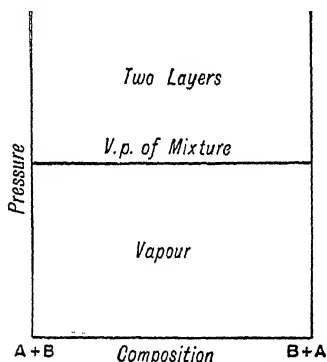
FIG. 69.   Vapour pressure diagram   FIG. 70.   Boiling point diagram
of immiscible liquids   of immiscible liquids

have the composition E. If the system has a composition between C and E, the layer of composition D will disappear during fractionation, and the boiling point will slowly rise to that of pure water. If, however, the system has a composition between E and D, the layer of composition C will disappear during fractionation, and the boiling point of the remaining homogeneous solution will rise zeotropically to that of pure isobutyl alcohol.

III. IMMISCIBLE LIQUIDS

Atom from atom yawns as far
As moon from earth, or star from star.—EMERSON

73. Constancy of Vapour Pressure and Boiling Point.—If the two liquids are perfectly immiscible, each exerts its own vapour pressure independently of the other liquid.

The vapour pressure-composition curve consists of a straight line drawn across the pc-diagram as shown in Fig. 69. If we have a mixture of water and chlorobenzene, each liquid will exert its own vapour pressure, and when the sum of these vapour pressures is equal to 760 mm. the mixture will boil. Accordingly, the boiling point-composition curve is also a straight horizontal line as indicated in Fig. 70.

When a mixture of two immiscible liquids is distilled, neither influences the vapour pressure of the other, and when the sum of their vapour pressures is equal to atmospheric pressure,
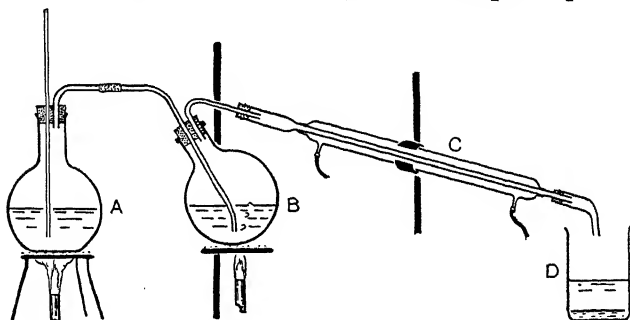
FIG. 71.   Steam-distillation

distillation goes on without change in the composition of the distillate until one of the liquid phases disappears. This constancy of boiling point and composition is in harmony with the Phase Rule, since a system of two liquid phases and a vapour phase is univariant. The relative weight of each liquid in the distillate will depend, not upon the respective amounts in the distillation vessel, but upon their relative vapour pressures and molecular weights.

74. **Theory and Practice of Steam-distillation.**—The process of steam-distillation is much used in preparative organic work for the separation and purification of high-boiling liquids and solids. It possesses a distinct advantage over ordinary distillation inasmuch as the material is not subjected to excessive temperatures and the danger of thermal decomposition is thus obviated or greatly minimised.

The organic material and water are placed in the flask B (Fig. 71) and, while the mixture is heated, steam from a separate generator A is passed through it at a fairly brisk rate. The evolved vapours, consisting of steam together with the

vapour of the organic substance, are condensed by means of a Liebig condenser C and collected in the receiver D. The substance is later separated from the aqueous layer by the usual methods. The process thus consists of the vaporisation of the substance in a current of steam, and in this way the involatile impurities are left behind as residue in the distillation flask.

The utility of the method is based on the following theoretical considerations :

Let us assume that the experiment is conducted at a pressure p (usually atmospheric).

Let p_1 and p_2 be the respective vapour pressures of water and the substance at the boiling point of the mixture. Then

$$p = p_1 + p_2.$$

Let M_1 and M_2 be the molecular weights of water and the substance, respectively.

The volumes of the vapours produced will be proportional to the partial vapour pressures, and the densities of the vapours will be proportional to their molecular weights.

If w_1 and w_2 are respectively the weights of water and of the substance which collect in the distillate, we have

$$\frac{p_1}{p_2} = \frac{w_1}{M_1} \Big/ \frac{w_2}{M_2}$$

$$\frac{w_1}{w_2} = \frac{p_1 M_1}{p_2 M_2}.$$

We see, therefore, that the weights of the two liquids collecting in the receiver are directly proportional to their vapour pressures and their molecular weights.

As an example let us consider the steam-distillation of iodobenzene C_6H_5I, which has the normal boiling point 188°. The vapour pressures of water and iodobenzene at different temperatures are given in the following table :

VAPOUR PRESSURE OF WATER AND IODOBENZENE

Tempera-ture	Vapour Pressure		
	Water	Iodobenzene	Mixture
70°	$p_1 = 233 \cdot 3$ mm.	$p_2 = 13 \cdot 6$ mm.	$p_1 + p_2 = 246 \cdot 9$ mm.
80°	354·9	21·8	376·7
90°	525·5	33·5	559·0
100°	760·0	50·2	810·2

If now we plot the values in the last column against the temperature we find from the curve so obtained (Fig. 72) that the vapour pressure of the mixture reaches 760 mm. at $98 \cdot 2°$; this is therefore the boiling point of the mixture. At this temperature we find $p_1 = 712 \cdot 3$ and $p_2 = 47 \cdot 7$ mm. The
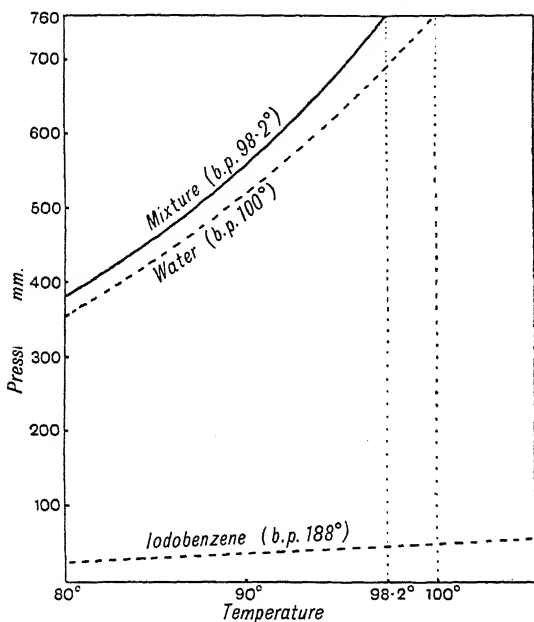
FIG. 72.   Theory of steam-distillation

molecular weights of the two liquids are 18 and 204, respectively. Substituting these values in the above equation, we have

$$\frac{w_1}{w_2} = \frac{712 \cdot 3 \times 18}{47 \cdot 7 \times 204} = \frac{13}{10}.$$

This indicates that for every 13 grams of water collected in the receiver we obtain 10 grams of iodobenzene. Although iodobenzene has only 1/15 of the vapour pressure of water at the boiling point of the mixture, yet 10/23 of the liquid collected is iodobenzene.

If an organic compound is chemically unaffected by water and possesses a vapour pressure of even 10 mm. or so at 100°,

distillation with steam for the purpose of isolation or purification will generally be repaid.   Its vapour pressure may indeed be merely a small fraction of that of water, but this effect is counterbalanced by the higher molecular weight with the result that appreciable quantities come over and condense with the steam.   The fortunate circumstance that the molecular weight of water is low renders it particularly suitable for vapour distillation in this way.

SUMMARY

Vapour Pressure and Distillation of Liquid Mixtures

Systems	pc-Curves	Character	Distillation	Example
Class I : COMPLETELY MISCIBLE Type I Zeotropic		Continuous; no maximum or minimum	Temperature rises continuously; can be fractionated into pure components	Benzene and toluene
Type II Azeotropic : Maximum b.p.		Curve has minimum. This mixture has maximum b.p.	Last distillate is mixture of maximum b.p. Cannot be fractionated	Formic acid and water; also HCl and water
Type III Azeotropic : Minimum b p.		Curve has maximum. This mixture has minimum b.p.	Can be separated into mixture of minimum b.p. and one or other of the pure components. Cannot be fractionated into the separate components	n-Propyl alcohol and water; also ethyl alcohol and water
Class II : PARTIALLY MISCIBLE		Curve has three parts horizontal, is univariant	Distils at constant temperature if two liquid phases are present	Isobutyl alcohol and water
Class III : IMMISCIBLE		Horizontal line, each liquid exerting its own vapour pressure unaffected by other	When sum of partial pressures equals 760 mm., mixture distils with constant distillate and b.p. Principle of steam-distillation	Iodobenzene and water

IV. THE THEORY OF SOLUBILITY

> But beyond the bright searchlights of science
>   Out of sight of the windows of sense,
> Old riddles still bid us defiance—
>   Old questions of Why and of Whence.
>
> <div align="right">—W. C. D. WHETHAM</div>

75. The Problem of Solubility.—Why are some substances soluble in certain liquids, yet refuse to dissolve in others ? Why does the solubility in certain liquids increase with temperature and decrease in others ?   Why are certain liquids miscible in all proportions, others partially miscible and others immiscible ?   It is even possible to obtain as many as six different liquid layers in a system consisting of hexane, aniline, water, phosphorus, gallium and mercury, as indicated in Fig. 73.   This is a stable system, and if the cylinder containing these substances is shaken, the layers will again separate on standing. What then gives rise to this remarkable display of "class distinction " or "molecular sociology " ? What are the factors which determine the non-mixing or unsociable attributes of the molecules of these various liquids ?

These are but a few of the perplexing problems which have long exercised the minds of chemists and physicists.   Progress has been undeniably slow since the days of the alchemists, who knew that " like dissolves like " (*similia similibus solvuntur*). In recent years, however, the researches of a large number of investigators, under the leadership of Hildebrand and of Kendall, have revealed some of the secrets of solution, and the new theory which is taking shape promises to render intelligible these commonplace but very remarkable phenomena.

What happens to the Solute ?—Owing to the close aggregation of molecules in the liquid state, intermolecular forces are strongly operative and these play a very important part in determining the behaviour of the molecules and the essential character of the liquid.   Until recently, it has been taken for granted that these intermolecular forces were either the ordinary van der Waals general attractions or actual valency forces producing definite associated molecules.   But it is now recognised

Fɪɢ. 73.   A stable system of six liquid layers

that the molecules may have dipoles and that these may also lead to association—dipole association—of the molecules.[1]

The van 't Hoff theory of ideal solutions was based upon the ingenious hypothesis that the solute in a dilute solution simulated the behaviour of a gas. The theory has been frequently misrepresented by some authors of standard text-books, who state that the solute in dilute solution is actually in the gaseous state. If indeed this were the case, a gas should have zero heat of solution, while the heat of solution of a liquid should be the heat of vaporisation and that of a solid the heat of sublimation. This is not true, and the assumptions are therefore untenable.[2]

FIG. 74.   The ideal solution obeys Raoult's law

The theory of ideal solutions developed by van Laar and elaborated by G. N. Lewis does not lend itself so readily to the confusion of hypothesis with reality. In the ideal case, where no complicating factors are involved, the heat of solution of a gas is equal to its heat of condensation, that of a liquid is zero and that of a solid is equal to its heat of fusion. This means that when a substance dissolves in a liquid the solute assumes the *liquid* state. Just as ice melts in an iced drink, so sugar may be said to melt when it dissolves in cold water.[3]

76. The Ideal Solution.—An ideal solution is one which obeys Raoult's law. This law states that the partial pressure of a constituent above a solution at a given temperature is equal to the molar fraction of the constituent in solution multiplied by the vapour pressure that constituent would have in the pure liquid state at the same temperature.

Thus suppose we have a binary solution of two components A and B in equilibrium with vapour as indicated in Fig. 74.

[1] Langmuir has even gone so far as to suggest that the entire ocean is just one large associated molecule and that pulling a fish from the sea is a dissociation process !

[2] Kendall, *Trans. Faraday Soc.*, 1937, **33**, 2.

[3] It is interesting to note that the Welsh have only one word, *toddi*, to signify " melting " and " dissolving ".

The total pressure of vapour will be $p_A + p_B$. Let the molar fraction of A in the liquid be $_L N_A$ and in the vapour $_V N_A$. Similarly, for component B let the molar fraction in the liquid be $_L N_B$ and in the vapour $_V N_B$. Stated mathematically, Raoult's law gives the relation between the partial pressure in the vapour phase and the vapour pressure of the pure liquid constituent—

$$p_A =_L N_A P_A \quad \text{and} \quad p_B =_L N_B P_B,$$

where P_A is the vapour pressure of the pure component A and P_B the vapour pressure of the pure component B.[1]

Raoult's law is based on two assumptions : (1) that the tendency of a molecule to escape from a liquid is measured by the pressure it exerts in the vapour phase, and (2) that the intermolecular forces are the same in both components of the mixture. If two substances satisfy these conditions they will form an ideal solution and there will be no volume change or heat effect (exothermic or endothermic) on mixing. Probably the best example of an ideal solution is a mixture of isotopes, since the intermolecular forces of the two isotopic species are practically identical.

Any deviation from Raoult's law must be due to a departure from the condition specified in one or in both of the above assumptions. Since the first assumption is based on the premise that the vapour behaves as a perfect gas and this is true for all practical purposes, it may be concluded that *intermolecular forces are the main cause of the deviations from Raoult's law.*

77. **Actual Solutions. Hildebrand's Theory.**—The pc-diagram representing the change in the partial vapour pressure of each component in a binary ideal solution is shown on p. 108. Deviations from Raoult's law are termed *positive* if the partial pressure lines lie above the ideal lines and *negative* if they lie below as shown in Fig. 75.

Positive deviations arise when the attraction between two molecules A and A is greater than between A and B. The attractive force between the molecules of a liquid sets up an " internal pressure ". Since this pressure may assume very high values it is much more important than the atmospheric or external pressure exerted on the liquid. If two liquids

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[1] Incidentally, the student will recall that Dalton's law gives the relation between the partial pressure in the vapour phase and the total pressure of the vapour phase, i.e. $p = p$

K

have the same internal pressure the mixture will obey Raoult's law. If their internal pressures are different there will generally be a positive deviation from the law. The mathematical argument in Hildebrand's theory [1] is based on the assumption that the deviations are proportional to the difference in the internal pressures. If the positive deviation is large, the total pressure curve will exhibit a maximum, corresponding to a minimum boiling point as in the case of alcohol and water.

Negative deviations arise when the attraction between a molecule of A and a molecule of B is greater than between
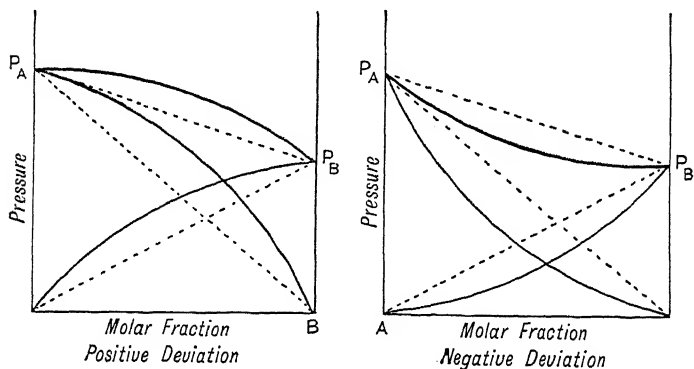
Fig. 75.   Deviations from Raoult's law

two molecules of A or two molecules of B—in other words, when there is a tendency towards compound-formation. If the negative deviation is large, the total pressure curve will show a minimum, corresponding to a maximum boiling point as exemplified by hydrogen chloride and water.

The main conclusions may be summarised according to the scheme :

POSITIVE DEVIATION

$$\left.\begin{array}{c} A \cdots A \\ B \cdots B \end{array}\right\} > A \cdots B$$
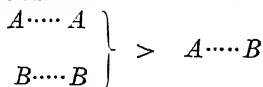
If the deviation is large the system becomes azeotropic with minimum boiling point.

NEGATIVE DEVIATION

$$A \cdots B > \left\{\begin{array}{c} A \cdots A \\ B \cdots B \end{array}\right.$$
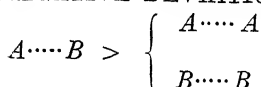
If the deviation is large the system becomes azeotropic with maximum boiling point.

[1] Hildebrand, *Solubility,* Reinhold Publishing Corporation, 1936.

78. **Partially Miscible Liquids.**—If the two components differ greatly as chemical individuals, the positive deviation from Raoult's law may be so great that the two liquids will be only partially miscible and form two layers.

The genesis of this condition is depicted in Fig. 76. The continuous lines represent the change in partial pressure of
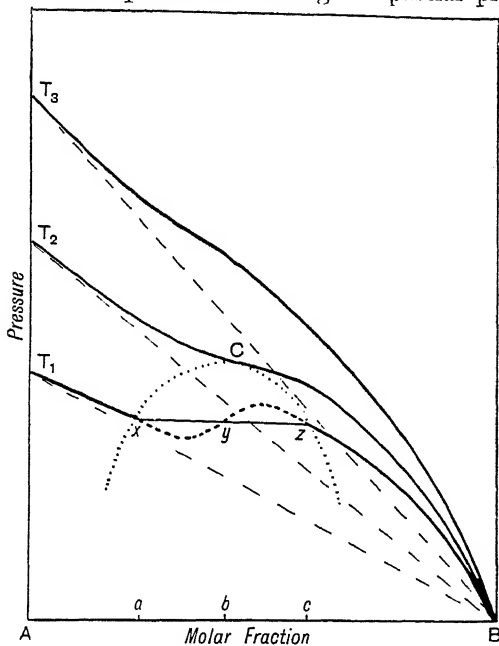
FIG. 76.   Hildebrand's theory of partial miscibility

component A with the molar concentration.   Three such curves are shown corresponding to three different temperatures T_1, T_2 and T_3.   At the highest temperature, T_3, the deviation is usually not so marked, but as we lower the temperature to T_2 the deviation becomes more pronounced, until at T_1 the partial pressure curve would show a maximum and a minimum, as indicated by the dotted S-shaped curve xyz.   Such a curve implies that the three different solutions represented by a, b and c should have the same vapour pressure.   But the existence of three such liquid phases in equilibrium is impossible according to the Phase Rule, and, actually, we find the system breaking up into two liquid layers of composition a and c,

respectively. This is reminiscent of the van der Waals pv-curve, where only the extreme values of the volumes can be realised experimentally.

As the temperature is raised the deviation from ideal behaviour becomes less and the points corresponding to x and z continue to approach one another. Finally, at a certain temperature, T_2, the points become coincident and merge at the point C. This is the critical solution temperature, which thus offers an analogy with the ordinary critical temperature of a liquid. At the critical temperature liquid and vapour become identical, while at the critical solution temperature the first liquid phase and the second liquid phase become identical.

The above theory provides a rational explanation of the fact that certain liquids have an upper critical solution temperature, but we have still to explain why other liquids have a lower critical solution temperature. We have just seen that lowering the temperature increases the positive deviation and this implies that the mutual solubility should also decrease. But we know that some liquids, like triethylamine and water or certain ketonic derivatives and water, exhibit quite the reverse behaviour and have a lower critical solution temperature. The explanation of this behaviour is to be found in the two opposing tendencies which are operative in these systems :

  (a) the positive deviation tending to decrease the mutual solubility at lower temperatures ;
  (b) compound-formation between the components tending to increase the mutual solubility at lower temperatures.

The stability of the complex $A\text{-}B$ will be greater the lower the temperature. At the lower critical solution temperature the combination between A and B (leading to the dissolution of B in A or A in B) becomes sufficiently powerful to outweigh the opposing tendency occasioned by the existence of positive deviation.

Little can be said as to the actual *modus operandi* of such compound-formation, but it is significant that substances which behave in this way have in their molecules a donor atom with a lone pair of electrons. The nitrogen atom in triethylamine Et_3N: and the oxygen atom of the ketonic group $>C\ddot{O}$ have lone pairs of electrons, which under suitable conditions can form a co-ordinate link or resonance bond with one of the hydrogen atoms of water.

The behaviour of nicotine and water, which have an upper

and a lower critical solution temperature, may also be explanied on similar lines.   Finally, it will be evident that when the two components are chemically quite dissimilar, the deviation from Raoult's law will be so great that they will remain immiscible, like water and mercury.

The main features of the Hildebrand theory as applied to liquid mixtures are indicated in the following summary.

SUMMARY

System	Positive Deviation	Negative Deviation
CLASS I : COMPLETELY MISCIBLE Type I. Zeotropic	$A\cdots A > A\cdots B$	$A\cdots B > A\cdots A$
Type II. Azeotropic: Maximum Boiling Point	..	Large
Type III. Azeotropic : Minimum Boiling Point	Large	..
CLASS II : PARTIALLY MISCIBLE	Great Leads to upper C.S.T., e.g. phenol and water. Opposed by compound - formation leading to lower C.S.T., e.g. triethylamine and water. Dual effect in nicotine and water system	..
CLASS III : IMMISCIBLE	Owing to very great deviation entirely dissimilar chemical species remain immiscible	..

PRACTICAL METHODS

13. Determination of Boiling Point of a Pure Liquid.—The normal boiling point of a liquid is the temperature at which the vapour pressure becomes equal to the external atmospheric pressure (760 mm. Hg). The particular method adopted for determining the boiling point will depend upon the amount of liquid available.

i. *Distillation Method.*—If 10-20 c.c. of the substance is available the boiling point is determined by distilling the

(a) Distillation method   (b) Siwoloboff's method   (c) Micro method
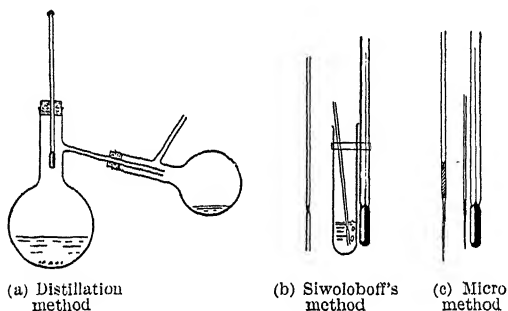
FIG. 77.   Determination of boiling point

liquid from a small distillation flask provided with a thermometer as shown in Fig. 77 (a). The following precautions must be duly observed :

(a) the bulb of the thermometer must be situated just below the side-tube of the flask ;

(b) the boiling must be regular—neither too slow nor too rapid—and the bulb of the thermometer must be completely enveloped in the vapour ;

(c) superheating, bumping and splashing of the liquid on to the bulb of the thermometer must be avoided.

Uniform ebullition may be ensured by adding a few pieces of porous pot or broken capillary tube to the liquid before the heating is commenced. When the distillation is proceeding regularly and the temperature has attained a steady value the thermometer is read. This is the boiling point under the prevailing external pressure, and is recorded as in the example —b.p. 80°/752 mm.

When it is necessary to make allowance for the normal pressure, the boiling point at 760 mm. may be calculated according to Craft's rule :

$$t_{corr.} = t_{obs.} + 0 \cdot 0001(273 + t_{obs.}) \times (760 - B),$$

where $t_{corr.}$ is the corrected boiling point, $t_{obs.}$ the observed boiling point and B the barometric pressure in mm.

ii. *The Escaping Bubble Method.*—This method, due to Siwoloboff, requires about 1 c.c. of the liquid. A narrow capillary tube is sealed at a point about 1 cm. from the end, as shown in Fig. 77 (b). About 1 c.c. of the liquid is placed in a small thin-walled test-tube which is attached to the thermometer by means of rubber bands. The capillary is inserted in the liquid, and the apparatus immersed in a bath which is heated slowly with good stirring.

As heat is applied, there will be a slow escape of air-bubbles from the end of the capillary, but when the boiling point of the liquid is reached, a rapid and continuous escape of vapour-bubbles will be observed. The reading of the thermometer when this occurs is the boiling point of the liquid. A more accurate value may be obtained by allowing the bath to cool slightly and noting the temperature at which no bubbles escape from and no liquid enters the capillary.

iii. *Micro Method.*—An accurate boiling point determination may be made with a fraction of a drop of liquid by means of the following micro method described by H. V. Briscoe.

A capillary tube of 1 mm. bore is drawn out to a hair-fine capillary and sealed at the bottom as shown in Fig. 77 (c). A little of the liquid is introduced so as to enclose a minute bubble of air in the lower part of the tube. The tube is attached to a thermometer and immersed in a bath provided with an efficient stirrer. On heating up the bath the imprisoned air-bubble expands slowly, but at the boiling point it suddenly increases in volume and drives the liquid to the level of the surface of the bath.

14. **Determination of Boiling Point of a Solution.**—The ordinary distillation method cannot be applied to determine the boiling point of a solution containing an involatile solute, since the composition of the vapour is not the same as that of the solution. Accordingly, the thermometer must be immersed in the solution or fixed in such a way that the boiling solution can be pumped over the thermometer bulb. Among

the many precautions which must be observed in ebullioscopic determinations of this kind we may note the following :

(a) superheating of the solution must be avoided ;
(b) the boiling must be regular ;
(c) no vapour must leave the system, since this would alter the concentration of the solution ;
(d) the cold condensate from the reflux condenser must not come into direct contact with the thermometer.

Although the well-known Beckmann apparatus has been extensively used for determining the boiling points of solutions

(a) Electrical heating method
(b) Lift pump method
(c) Circulating pump method
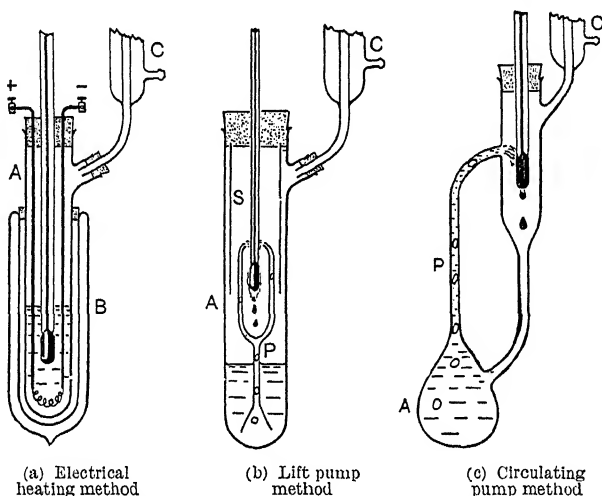
FIG. 78.   Determination of the boiling point of a solution

and the molecular weight of solutes, it is now customary to employ one of the following methods according to the needs of the particular investigation.

i. *The Electrical Heating Method* (*Bigelow*).[1]—The apparatus (Fig. 78 (a)) consists of the boiling vessel *A*, fixed centrally in a Dewar vacuum flask *B* to avoid the effects of draughts. The side-tube of the boiling vessel is attached to a short reflux condenser *C*. The vessel is provided with a cork through which pass a thermometer and two stout copper wires connected to a spiral of platinum wire. These copper leads are connected through a sliding resistance to a series of

[1] *Amer. Chem. J.*, 1899, **22**, 280.

batteries, and a known weight W of the pure solvent is heated by passing a suitable electric current through the platinum spiral. When the liquid is boiling regularly and the temperature is steady, the thermometer is read and this is taken as the boiling point of the solvent.

The solution is then made by adding a known weight w of the solute and the boiling point determined as before. Further quantities of the solute may be added and the boiling points of more concentrated solutions found in the same way. If the solute is non-volatile, the molecular weight of the solute can be calculated from the formula

$$M = \frac{Kw}{eW},$$

where K is the ebullioscopic constant, e the elevation of boiling point, w the weight of solute and W the weight of solvent.

ii. *The Lift Pump Method (Cottrell)*.[1]—In this method the thermometer is suspended in the vapour phase and the solution pumped over the bulb by means of a lift pump. The apparatus (Fig. 78 (b)) consists of a boiling vessel A in communication with a reflux condenser C. The pump P is made from narrow glass tubing and the funnel-shaped end is arranged to rest on the bottom of the boiling vessel. The liquid is heated by placing a small flame a few centimetres below the vessel. When the liquid reaches the boiling point, bubbles of vapour are formed under the pump funnel, and the liquid is lifted through the pump and ejected at the top on to the thermometer. In this way the thermometer bulb is bathed with the boiling liquid and the film of solution is in equilibrium with the vapour in the apparatus. A glass shield S serves to insulate the central part of the system and reduce errors due to draughts.

The pumping device is undoubtedly the most successful improvement yet introduced into practical ebullioscopy, since it avoids almost entirely the errors due to superheating.

iii. *The Circulating Pump Method (Swietoslawski)*.[2]—This method embodies the Cottrell principle and merely differs in the arrangement for pumping the solution over the bulb of the thermometer, as shown in Fig. 78 (c). When the liquid in the bulb A is gently boiled, bubbles of vapour rise through the vertical tube P and cause some of the liquid to be ejected

[1] *J. Amer. Chem. Soc.*, 1919, **41**, 721.

[2] *Bull. Soc. Chim.*, 1931, 1563. *Ebulliometry*, Spon & Co., 1937.

over the thermometer bulb. This simple apparatus gives accurate results and is very suitable for students.

iv. *The Differential Thermometer Method (Menzies).*[1]— This is the best method of determining slight differences in the boiling points of solutions and of finding the molecular weight of a solute by the ebullioscopic method. It makes use of a differential thermometer charged with water, so that the errors inherent in the metastatic type of thermometer are avoided.

The differential thermometer, which measures the difference in temperature existing simultaneously at different points,

FIG. 79. Menzies' apparatus

is illustrated in Fig. 79. It consists of a U-tube charged with water in contact with its vapour, all air having been removed prior to sealing. The two limbs are graduated in millimetres. If the bulbs *a* and *b* are at the same temperature the difference in level of the water will be merely that due to capillarity, but if the temperature of *a* is higher than that of *b* the pressure of vapour in the two bulbs will be different, and this will cause a change in the level of the liquid. We can read off this difference and find from the Menzies tables the difference of temperature which caused it.

The ebullioscopic apparatus consists of a graduated boiling vessel *A*, a vapour chamber *B*, a condenser *C*, the differential thermometer *D* and its supporting extension *E*, and a Cottrell pump *P*.

Before the actual experiment is commenced, the boiling point of the pure solvent is taken by hanging a good ordinary thermometer in the vessel. The liquid is boiled and the steady temperature recorded. The actual working volume of the solvent is then found by swinging aside the flame (not lowering the gas), bringing up a beaker of cold water to touch the bottom of the vessel to stop the bubbling, and then reading the volume of liquid before the excess solvent drains from the walls.

The flame is swung back into position and the thermometer withdrawn. The pump is lowered on a hook to the bottom of the vessel and the differential thermometer introduced to

[1] *J. Amer. Chem. Soc.*, 1921, **43**, 2309 ; *ibid.* 2314.

engage with the pump as shown in Fig. 79. The solvent is boiled again and the difference of level in the differential thermometer noted. This is termed the zero reading h_1. A weighed pellet of the solute is then dropped through the condenser and the new difference in level h_2 caused by the boiling solution is observed. The value $h_2 - h_1$ is the ebullioscopic rise in terms of the vapour pressure of water, and this is converted into actual degrees by the use of the tables. In the case of benzene, for example, we can use the following table which gives for each tenth of a degree the change of temperature corresponding to 1 mm. change in the level of water in the differential thermometer.

°C.	0·0°	0·1°	0·2°	0·3°	0·4°	0·5°	0·6°	0·7°	0·8°	0·9°
80	0·004969	4952	4935	4918	4901	4884	4867	4851	4834	4817
81	0·004800	4784	4767	4751	4735	4719	4702	4686	4670	4654
82	0·004638	4623	4617	4592	4576	4560	4545	4530	4514	4499

This method gives molecular weight results accurate to within 0·5 per cent.

15. **To Fractionate a Mixture of Liquids.**—The fractional distillation apparatus is assembled as shown in Fig. 59 and the fractionation of benzene and toluene, or benzene and xylene conducted as described on p. 112.

16. **Preparation of Standard Hydrochloric Acid.**—Commercial concentrated hydrochloric acid is diluted with water so that its density is 1·10 as determined with a hydrometer. The solution is introduced into an ordinary distillation apparatus and three-quarters of the liquid is distilled off. The remainder is distilled into another receiver and the distillate thus obtained is the constant boiling mixture.[1]

At 760 mm. the constant boiling mixture boils at 108·6°, and its density at 25° is 1·09620. It contains 20·22 per cent of hydrochloric acid, so that a normal solution is obtained by diluting 164·42 c.c. or 180·170 g. of the constant boiling mixture to a litre. The liquid is not hygroscopic, so that a normal solution may be prepared with an accuracy seldom attained by other methods even with very elaborate precautions.

The following figures give the composition of the constant boiling mixture under different pressures of distillation :

[1] Hulett and Bonner, *J. Amer. Chem. Soc.*, 1909, **31**, 390.

Pressure	Composition of Constant Boiling Mixture
mm.	Per cent.
770	20·218
760	20·22
750	20·290
740	20·314

Evidently, therefore, it is only for the most accurate precision work that allowance need be made for small variations from the normal atmospheric pressure.

17. **To investigate a Maximum Boiling Azeotropic Mixture.** —A litre distilling flask is connected to a condenser through which water is circulated as in an ordinary distillation. The neck of the flask is closed by means of a rubber stopper through which passes a thermometer graduated in tenths of a degree, and arranged with the bulb below the side-tube of the flask so that the scale is visible between 100° and 110°. A set of twelve test-tubes labelled D_1, D_2, D_3... as well as a similar set labelled R_1, R_2, R_3... are also prepared.

Five hundred c.c. of a 10 per cent solution of hydrochloric acid is placed in the flask together with a few pieces of porous pot to prevent bumping. The flask is heated with a naked flame (this also prevents superheating) and the liquid distilled at a fairly rapid but uniform rate. The first 10 c.c. or so of the distillate is collected in a general receiver while the thermometer is warming up to equilibrium. The test-tube D_1 is then placed to catch about 4 c.c. of the distillate and the thermometer read while this sample is being collected. The flame is now removed and a 5 c.c. sample of the residue in the flask pipetted into the test-tube R_1. The two test-tubes are tightly stoppered and set aside to await analysis.

The distillation is now resumed using the same flame as before and the distillate collected in the general receiver until the thermometer has risen about a degree. The test-tube D_2 is now arranged to catch another 4 c.c. sample of the distillate and the temperature again noted. The flame is removed and a 5 c.c. sample of the residue taken and introduced into the test-tube R_2.

The experiment is continued along these lines, samples of distillate and residue being collected at observed temperatures until about 10 c.c. of liquid remains in the flask.

The concentration of hydrochloric acid in the distillate samples and in the residue samples is then determined by titrating 1 c.c. amounts with standard ($N/5$) alkali.

The temperatures are plotted as ordinates and the percentages as abscissae, and the position of the maximum boiling mixture located from the curves as indicated in Figs. 63 and 64.

18. **To investigate a Minimum Boiling Azeotropic Mixture.**— A convenient apparatus for the study of azeotropic mixtures is shown in Fig. 80. It consists of a 500 c.c. Claisen flask A with one neck carrying a thermometer and the other a sampling
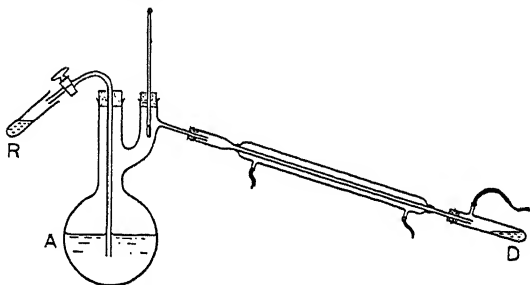
Fig. 80. Apparatus for investigation of azeotropic mixtures

tube for introducing the liquid into the " residue receiver " R. The flask is connected to a condenser with its lower end attached to the " distillate receiver " D.

Acetone and methyl alcohol are suitable liquids for use in this experiment. A known volume (225 c.c.) of pure acetone is placed in the Claisen flask and the boiling point determined. The distillate of pure liquid is returned to the flask and 25 c.c. of methyl alcohol added. The mixture is boiled at such a rate that 2-3 drops of distillate pass over per second into a graduated cylinder which serves as general receiver. The cylinder is removed and the receiver D_1 attached to the condenser. After 5 c.c. of distillate has been collected the temperature is recorded. A sample of the residual liquid in the Claisen flask is now taken. For this purpose, the stopcock is opened and 5 c.c. of liquid forced over into the receiver R_1 by blowing through the rubber tube attached to the side-tube of the distillate receiver. The whole operation requires only a few seconds and samples are taken without interrupting the boiling process. The tubes are stoppered and set aside to await analysis.

Twenty-five c.c. of methyl alcohol is then added to the flask and the distillation continued as before, the distillate samples D_2, D_3, D_4, etc. and the residue samples R_2, R_3, R_4, etc., being collected at observed temperatures t_2, t_3, t_4, etc. When the temperature of the vapour approaches that of pure methyl alcohol the experiment is interrupted, the flask charged with this liquid and its boiling point determined.

The analysis of the samples is easily made by measuring (a) the density, (b) the refractive index, or (c) the surface tension. The du Nuoy Surface Tension apparatus is very convenient for this purpose and the composition of the sample is readily found from a previously prepared surface tension-composition curve.[1]

When the compositions of the series of vapour fractions and residue fractions are plotted against the corresponding temperature of distillation we obtain the vaporus and liquidus curves of the general form shown in Fig. 66.

19. **To Study the Principles of Steam Distillation.**—The apparatus is assembled as shown in Fig. 71, but for the purpose of the present experiment a thermometer is also placed in the neck of the flask B.

The preliminary part of the experiment consists in finding the boiling point of water under the prevailing pressure. For this purpose 25 c.c. of water is placed in the flask B and steam passed through it at a rapid rate until it boils. When the thermometer is steady the temperature is read, and this is taken as the boiling point of water under the prevailing conditions.

The actual experiment is conducted as follows. Three hundred c.c. of chlorobenzene and 25 c.c. of water are introduced into the flask B. The steam-generator is heated with a fairly strong flame, while the distillation flask is heated with a small flame until it is thoroughly hot and steam no longer condenses in it. After neglecting the first 20 c.c. of the distillate, three separate 100 c.c. samples are collected at observed temperatures in graduated cylinders. The distillation should be carried out at constant temperature and this will be the case so long as a steady current of steam is passing through the organic liquid.

After allowing the distillates to stand overnight (so that the separation into two layers is complete) the volumes of

[1] Soday and Bennett, *J. Chem. Education*, 1930, **7**, 1336.

chlorobenzene and water in each cylinder are measured.   The density of water at 18° is 0·9999 and that of chlorobenzene is 1·110, so that the weight of water w_1 and that of chloro-benzene w_2 may be calculated.   The vapour pressure of water p_1 and that of chlorobenzene p_2 at the temperature of distillation are found from vapour pressure tables.   It may be shown that $w_1/w_2 = p_1 M_1/p_2 M_2$, where M_1 and M_2 are the molecular weights of water and chlorobenzene respectively. Alternatively, the molecular weight of chlorobenzene may be calculated from the above equation.

Other liquids which may be used instead of chlorobenzene are bromo-benzene and nitrobenzene.

20. **Determination of Moisture by Entrainment Distillation.**—The water content of " air-dry " drugs and other materials of vegetable origin is relatively high and the residual moisture can seldom be accurately determined by the process of simple drying.   The modern practice of moisture determination by distillation [1] is based on the fact that when a moist solid is heated in a boil-ing liquid with which water is immis-cible, the water is carried over with the organic vapour and the volume of the

Fig. 81.   Entrainment distillation appara-tus for moisture de-termination

aqueous layer in the condensate is a direct measure of the moisture in the original solid sample :

$$\text{Solid}/\text{H}_2\text{O} + \text{Liquid} \qquad \text{Dry Solid} + \text{Liquid}/\text{H}_2\text{O}.$$

The entrainment distillation apparatus developed by the Government Laboratory [2] is illustrated in Fig. 81.   A known weight of the solid sample (yielding about 2 c.c. of water) is placed in the flask together with a few silica beads to prevent bumping and, if necessary, some sand to prevent caking.   After covering the sample with an inert organic liquid such as

[1] Tate and Warren, *Analyst*, 1936, **61**, 367.

[2] Obtainable from Messrs. Griffin & George, Ltd., Ealing Road, Alperton, Wembley, Middlesex.

heptane which boils at 99-100°, the apparatus is assembled as shown and sufficient heptane is poured down the condenser to fill the graduated portion of the receiver.   The flask is now heated in an oil-bath or air-oven, and the water carried over in the vapour condenses and collects in the graduated tube. When the distillation is complete the volume of the aqueous layer is a measure of the water content of the solid material.

The method may be applied to determine the moisture content of cocoa, yeast, artificial silk yarn, etc.

QUESTIONS

1. Discuss the relationship between composition and partial vapour pressures of two completely miscible liquids.   What bearing has the relationship upon the possibility of separating two such liquids by fractional distillation ?   (Cambridge Tripos.)

2. Give an account of the typical diagrams showing the relation between concentration and temperature (b.p.) for mixtures of two completely miscible volatile liquids.   Discuss the behaviour on distillation of such mixtures and refer to any examples exhibiting special points of interest.   (Sub. B.Sc., Birmingham.)

3. Propyl alcohol and water are miscible in all proportions. The vapour pressure curve passes through a maximum corresponding to a mixture containing about 80 per cent of propyl alcohol.   The corresponding curve for formic acid passes through a minimum at 75 per cent of formic acid.   Compare the behaviour on distillation of aqueous solutions containing 50 per cent of formic acid and propyl alcohol respectively.

(B.Sc., Sheffield.)

4. Two liquids A and B are miscible in all proportions. Indicate with the help of diagrams the behaviour of a mixture of A and B on distillation (a) if only one component can be separated in the pure state, and (b) both components can be separated.   What are the principles involved in the use of fractionating columns for distillation ?   (B.Sc., Manchester.)

5. Describe how you would treat a mixture of water, alcohol and ether in order to recover the alcohol and ether.
State how the alcohol could be made absolute and the ether freed from traces of water and alcohol.

(B.A., Cape of Good Hope.)

6. Show by means of curves how (a) the pressure, (b) the composition of the vapour alters with the composition of the

liquid phase in different types of mixtures of two liquid com-
pounds. By means of them explain the existence of mixtures of
constant minimum and maximum boiling point.

(B.Sc., Special, London.)

7. Give an account with illustrative examples of (a) mixtures
of constant boiling point and (b) distillation in steam. What are
the advantages of the latter processes ?

The immiscible liquid system aniline-water boils at 98° under
a pressure of 760 mm. At this temperature the vapour pressure
of water is 707 mm. If this system is distilled in steam what
fraction of the total weight of the distillate will be aniline ?

(Higher Certificate, Central Welsh Board.)

8. " Distillation is one of the most valuable methods at the
disposal of the organic chemist." Discuss this statement with
respect to fractional distillation and distillation in steam. Explain
the principles underlying these processes and describe in detail
the apparatus necessary for efficiency.

(Higher Certificate, Joint Matriculation Board.)

9. Describe and explain the operation known as distillation in
steam. When aniline (mol. wt. 93) is steam-distilled the distillate
is found to contain 26·5 per cent by weight of aniline. What is
the approximate vapour pressure of aniline at the temperature of
distillation ?

(Higher Certificate, Oxford and Cambridge Exam. Board.)

10. Explain the process of steam distillation as applied to the
determination of molecular weights. A mixture of water and
bromobenzene was found to boil at 95·2°, at which temperature
the vapour pressure of water is 639·7 mm. The barometric
pressure was 760 mm. and the distillate was found to contain
47·4 per cent by volume of water. Calculate the molecular
weight of bromobenzene, its density being 1·516.

(Sub. B.Sc., Birmingham.)

11. Two non-miscible liquids, toluene and water, are distilled
together from an ordinary distillation flask under a barometric
pressure of 755 mm. From the vapour pressures of the two pure
liquids given below, calculate (a) the boiling point of the pair of
liquids, (b) the composition of the distillate :

Temperature			83°	84°	85°	86°
V.p. of Water	.	.	400·1	416·3	433·0	450·3
V.p. of Toluene	.	.	321·7	332·7	344·7	355·7

(Moderatorship, Dublin.)

12. How would you proceed to calculate the boiling point of a
mixture of water and a liquid immiscible therein ? Show how
this is applied in practical chemistry and explain why it may be
so applied.   (Associateship, Institute of Chemistry.)

13. Discuss the vapour pressure curves of the following systems, (a) toluene and water, (b) propyl alcohol and water, (c) hydrogen chloride and water.   How would these systems behave in distillation ?   (B.Sc., Manchester.)

14. Give a general account of the way in which the vapour pressure of a mixture of two liquids varies with the composition. How far can the various types of behaviour be explained ?

(Final Honours, Oxford.)

LIQUID AND SOLID PHASES

. . . and order from disorder sprung.
Swift to their several quarters hasted then
The cumbrous elements.—MILTON

79. **The " Reduced " Phase Rule.**—The effect of pressure on the equilibrium between liquids and solids is usually very small. When therefore a system consists of liquid and solid phases only, the effect of pressure may be disregarded and it is only necessary to take into account the other variables, viz. temperature and concentration. Since the experiments are usually conducted under atmospheric pressure, and the vapour pressures of solids and their melts are very low, such a system of solid and liquid phases is termed a *condensed system*. In the case of these condensed systems we may disregard the pressure factor for all ordinary purposes and concern ourselves solely with the remaining degrees of freedom, so that we may write a " reduced " Phase Rule

where F′ gives the remaining degrees of freedom of the system.

It is claimed that the " reduced " Phase Rule is more convenient to apply to the equilibria between solid and liquid phases, and facilitates especially the discussion of alloy systems.[1] It must not be overlooked, however, that the implicit assumption is made that the external pressure is large in comparison with the actual vapour pressure of the components, and it is only when this condition is fulfilled that the " reduced " Phase Rule may be applied to determine the number of degrees of freedom of the system.

[1] There is really no need to reduce the Gibbs Phase Rule to a simpler form. Actually, as the student can test for himself, it is just as easy (and certainly more correct) to apply the ordinary Phase Rule to these equilibria. In view of the prevailing custom, however, we shall make use of the " reduced " form in discussing condensed systems of this kind.

80. **Classification of the Systems.**—The equilibrium diagram may belong to one of several types according to the nature of the components, and the various systems may be classified as follows :

CLASS I. EUTECTIC SYSTEMS.

Type I (*a*). Formation of Simple Eutectic.
Type I (*b*). Formation of Monotectic.
Type II.   Formation of Compound with Congruent Melting Point.
Type III.   Formation of Compound with Meritectic or Incongruent Melting Point.

CLASS II. COMPLETELY MISCIBLE SOLID SOLUTIONS.

Type I.   Continuous Series of Solid Solutions.
Type II.   Minimum Melting Solid Solution.
Type III.   Maximum Melting Solid Solution.

CLASS III. PARTIALLY MISCIBLE SOLID SOLUTIONS.

Type I.   Peritectic System of Two Solid Solutions.
Type II.   Eutectic System of Two Solid Solutions.

I. EUTECTIC SYSTEMS

81. **Type I (a). Formation of Simple Eutectic.**—Let us consider the general case of two components, A and B, which neither combine to produce a compound nor form a solid solution by dissolving in each other in the solid state.

The equilibrium diagram for such a system is shown in Fig. 82, where the point A represents the melting point of the pure component A and the point B that of the pure component B. Usually, the freezing point of a liquid is lowered by dissolving another substance in it, so that the addition of component B to component A will cause the temperature of equilibrium or the freezing point to be lowered.[1] This is shown by the curve

[1] The fact that the presence of a " foreign ingredient " lowers the melting point of a substance forms the basis of the so-called " mixed melt " test for the identification of organic compounds. Thus, suppose we are given an unknown substance A which we suspect to be benzoic acid because its melting point is found to be 121°. To test the correctness of this supposition we procure a small amount of an authentic specimen of benzoic acid and thoroughly mix it with roughly the same

AC, which represents the compositions of solutions in equilibrium with the solid component A at different temperatures. Similarly, the curve BC shows the effect of adding component A to component B, the freezing point or temperature of equilibrium being lowered along BC.

At C, the point of intersection of the two curves, the two solid components can exist in equilibrium with a liquid solution of composition represented by the point C. This point is called the *eutectic point* [1] and represents therefore
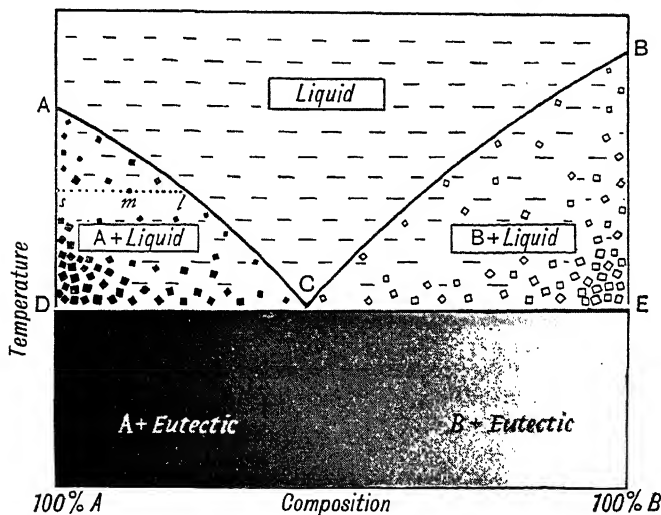
FIG. 82.   Simple eutectic system

the temperature and composition at which the system, solid A/solid B/liquid, can exist in equilibrium.   In other words, the eutectic point gives the temperature and composition of the system when both components crystallise out simultane-

amount of A, and then determine the melting point of the mixture. If the melting point is still 121°, then A must be benzoic acid, but if the melting point is several degrees lower, then A cannot be benzoic acid.

The test, though of great practical use, is not infallible, since in some cases, where a solid solution or mixed crystal is formed, the melting point of the mixture may be raised.   A few cases are also known where the melting point of one component is not affected by the dissolution of another component.

[1] The word *eutectic* is derived from the Greek meaning *easy melting*.

ously. This solid mixture is called the *eutectic mixture*. It has a fixed and definite composition, and melts and freezes in the manner of a pure substance at a fixed temperature. This temperature is the eutectic temperature, which is invariably the lowest freezing point of the whole series. To this phenomenon the name *eutexia* is sometimes applied and its occurrence is in complete harmony with the predictions of tne " reduced " Phase Rule :

$$P + F' = C + 1,$$
$$3 + F' = 2 + 1.$$
$$F' = 0.$$

Accordingly, if the experiment is carried out under constant atmospheric pressure, neither the temperature nor the composition corresponding to the point C can be altered without changing the number of phases.

Although the eutectic mixture possesses the attributes of definite composition and definite melting point, it is not to be regarded as a chemical compound because (a) it seldom corresponds to the calculated composition of a simple chemical compound, and (b) separate crystals of the two components can be seen under a microscope. It is, in fact, nothing more than an intimate mechanical mixture or crystalline conglomerate of the two components.

Liquidus and Solidus.—In discussing these systems, the temperature at which solid begins to crystallise from the liquid solution will be designated the *freezing point* of the mixture, and the temperature at which the solid mixture begins to liquefy will be called the *melting point*. The complete equilibrium diagram generally includes two curves, which are termed liquidus and solidus. The *liquidus* is the temperature-concentration curve of the liquid phase ; it is therefore the freezing point curve and corresponds to the " beginning of freezing ". The *solidus* is the temperature-concentration curve of the solid mixture ; it is therefore the melting point curve and corresponds to the " end of freezing " on cooling or the " beginning of melting " on heating the system.

In the system under consideration (Fig. 82) the liquidus curves are AC and BC, while the solidus curves comprise the horizontal line DE of constant eutectic temperature and the vertical lines DA and EB. These curves divide the diagram into areas or regions which harbour the phases indicated therein, and it is easy to read off the composition of the system

represented by any point in the diagram. Thus the point m represents a mixture of solid A (i.e. composition s) and liquid of composition l; the amount of solid in the mixture is given by lm/ls.

If we apply the " reduced " Phase Rule to a system represented by a point on the liquidus we have

$$2 + F' = 2 + 1,$$

so that the system is univariant. Similarly, a system represented by a point above the liquidus will consist of one liquid phase, so that

$$1 + F' = 2 + 1,$$

and the system is bivariant with respect to temperature and concentration.

82. **Gold and Thallium.**—Gold melts at 1064°, thallium at 303°, and the two metals give a eutectic point at 131°. In
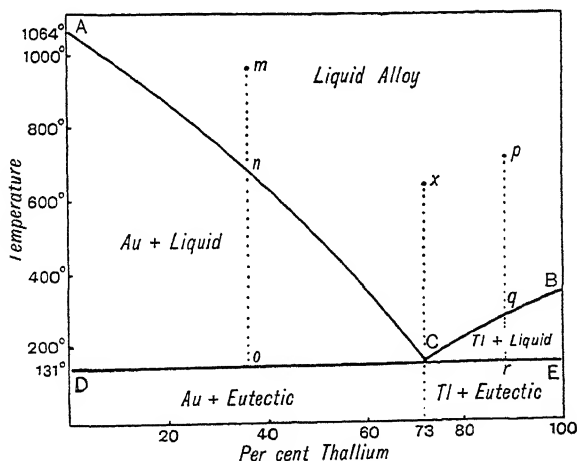
FIG. 83. Eutectic system of Gold and Thallium

Fig. 83 the liquidus ACB shows the lowering of the freezing point by the addition of one component to the other. All alloys of gold and thallium above the liquidus are wholly liquid, while all alloys below the solidus DE are wholly solid. Between the solidus and the liquidus the alloy is partly solid and partly liquid—actually, a mush or paste of the two phases.

The eutectic mixture consists of 73 per cent of gold and 27 per cent of thallium. Every solid alloy consists either of the exact eutectic mixture or of the eutectic mixture plus free crystals of gold or of thallium.[1] If the solid alloy has the exact eutectic composition it will liquefy as a whole at the constant temperature of 131°. On the other hand, if the solid alloy does not possess this particular composition the eutectic portion of it will still liquefy at this temperature when heated. In other words, the gold and the thallium will melt together in the eutectic proportions at constant temperature until one of the components is completely liquefied. At this stage, therefore, we have the liquid eutectic mixed with solid gold or with solid thallium, and all the solid will not disappear until the system has been heated to a point on the liquidus.

Let us now consider the phase changes which occur on cooling down a liquid alloy of composition and temperature represented by the point m. When the temperature falls to the point n on the liquidus AC, gold will crystallise out. As the temperature is lowered further, more and more gold separates out and the composition of the solution (becoming higher in thallium) will alter in the direction of C. When the temperature has fallen to the point o on the solidus DE, the liquid has now the composition of the point C and thallium can now begin to crystallise out. At this stage there will be simultaneous crystallisation of gold and thallium and the temperature will remain constant until the whole system has solidified. Then and then only does the temperature fall again.

Similarly, if we cool down a system represented by the point p the liquid alloy will begin to deposit crystals of thallium at the point q on the liquidus BC, and the composition of the solution (becoming higher in gold) will advance towards C. When the solution has attained the eutectic composition, both thallium and gold crystallise out as a eutectic conglomerate and there is no further fall in temperature until the whole system is solid at r.

If, however, the system possesses the exact eutectic composition, as at x, neither solid will crystallise out until the eutectic temperature is reached. When the temperature has fallen to this point, the two components separate out side by

[1] In fact the gold-thallium system has been chosen for discussion because it approaches very closely the ideal system in which no solid solutions are formed.

side as the eutectic mixture and the temperature remains constant until the whole liquid is converted into solid.

The Pattinson Process.—With regard to the phenomena described above, it may be recalled that the Pattinson process for the desilverisation of lead was based on the fact that a dilute solution of silver in lead deposits pure lead on cooling to the freezing point and the liquid portion becomes richer in silver. As formerly practised the operations were carried out in a series of thirteen pans, the argentiferous lead being melted in pan No. 7 and allowed to cool until two-thirds of the lead had crystallised. The crystals, now poorer in silver, were transferred by means of a perforated ladle to pan No. 6, while the liquid portion, now richer in silver, was removed to pan No. 8. This process was repeated for each pan, the purer lead crystals being transferred in one direction and the richer silver-lead alloy in the other direction. Finally, the extreme pan No. 1 contained pure lead, while pan No. 13 contained a 1·8 per cent silver-lead alloy. This material, containing about 3 lbs. of silver per ton, was further refined by

Fig. 84. Monotectic system of Tin and Silicon

cupellation, the lead being oxidised to litharge, which was easily removed from the liquid silver.

The simple eutectic system is naturally the most common of all the systems met with in practice and other examples of this type are copper and silver, naphthalene and phenanthrene, naphthalene and *p*-toluidine and potassium chloride and silver chloride.

83. Type I (b). Formation of Monotectic.—An extreme case of the simple eutectic system is obtained when the liquidus rises continuously from the melting point of component *A* to that of component *B* and the solidus is a horizontal line through the melting point of *A*. In these circumstances the solidus is called a *monotectic* and the system a monotectic system.

An example of this type is afforded by the alloys of tin and silicon which give the phase diagram shown in Fig. 84. Tin

melts at 232° and silicon at 1420°. The liquidus AB rises continuously to the melting point of pure silicon, while the solidus or monotectic is the horizontal line AM.

If we cool a liquid alloy from the point a it deposits crystals of pure silicon at b and the deposition of this element continues as the temperature falls to 232°. During this process the liquid becomes richer in tin and the composition of the liquid phase changes along the curve bA. At 232° the system consists of pure liquid tin and solid silicon in the ratio $cM : cA$. The liquid tin then solidifies at constant temperature so that a sheath or coating of solid tin is deposited around the crystals of silicon already present. The monotectic may thus be regarded as a eutectic of tin and silicon in which the amount of silicon is infinitely small.

84. **Type II. Formation of Compound with Congruent Melting Point.**—A substance is said to have a congruent melting point when it is capable of existing as a stable solid in equilibrium with a liquid of the same composition :

$$S \qquad \text{liquid.}$$

All ordinary melting points are congruent in the sense that the composition of the molten liquid is the same as that of the solid from which it is derived. When two components combine to form a stable compound the latter will constitute a separate solid phase and will thus have an equilibrium curve of its own in conformity with the rule "New phase—New curve ".

(a) *Benzophenone and Diphenylamine.*—The equilibrium diagram for benzophenone $(C_6H_5)_2CO$ and diphenylamine $(C_6H_5)_2NH$ is shown in Fig. 85. The point A represents the freezing point of benzophenone (47·7°) and B that of diphenylamine (52·8°). When diphenylamine is added to benzophenone the freezing point is lowered along the curve AC. At C (31·9°) we have the first eutectic point where benzophenone and the addition compound $[(C_6H_5)_2CO . (C_6H_5)_2NH]$ separate out together as a eutectic conglomerate. The further addition of diphenylamine progressively raises the freezing point until at D (40·2°) the curve reaches its maximum. At this point the composition of the liquid phase is identical with that of the solid phase and this maximum temperature is therefore the congruent melting point of the compound $[(C_6H_5)_2CO . (C_6H_5)_2NH]$.

Similarly, the freezing point of diphenylamine is lowered

by the addition of benzophenone as represented by the curve *BE*. The point *E* is the second eutectic point, where there is separation of a eutectic mixture of diphenylamine and the compound $[(C_6H_5)_2CO.(C_6H_5)_2NH]$. The addition of more benzophenone will cause the temperature of equilibrium to rise along *ED* until the melting point of the compound is reached as before.

The liquidus consists of the curves *AC*, *CDE* and *EB*, while the solidus comprises the horizontal lines *FG* and *HJ*
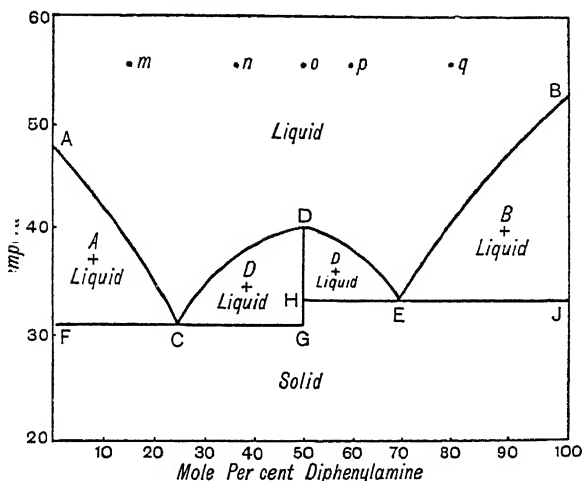
FIG. 85.   Benzophenone and Diphenylamine

as well as the vertical lines *FA*, *GD* and *JB*. The areas have the significance indicated in the diagram. It is evident that the presence of a stable compound is marked by

(1) a maximum point on the liquidus ;
(2) a meeting point of solidus and liquidus ;
(3) the existence of a eutectic point on either side.

The behaviour of various systems on cooling is readily predicted from the diagram :

System.		*Phases in Order of Appearance on Cooling*
m	.	benzophenone, eutectic (benzophenone/compound),
n	.	compound, eutectic (benzophenone/compound),
o	.	compound only,
p	.	compound, eutectic (compound/diphenylamine),
q	.	diphenylamine, eutectic (compound/diphenylamine).

If the system has a composition corresponding to the points C, D or E, it will freeze as a whole at constant temperature. In all other cases, however, the mixture will freeze over the range of temperature between the liquidus and the horizontal solidus lines.

(b) *Magnesium and Zinc.*—As an example of a metallic system in which a compound is formed we may consider the
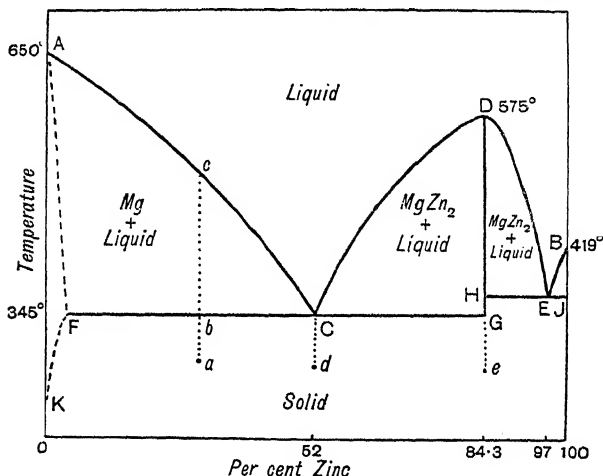
FIG. 86.   Magnesium and Zinc forming the compound MgZn$_2$

alloys of magnesium and zinc (Fig. 86). Magnesium melts at 650° and zinc at 419°. The two metals form a compound MgZn$_2$ with a true melting point at 575°.

The liquidus consists of four curves : AC showing the lowering of the freezing point of magnesium by zinc, DC the lowering of the freezing point of the intermetallic compound by magnesium, DE the lowering of the freezing point of the compound by zinc and BE the lowering of the freezing point of zinc by magnesium. There are two eutectic points : at C the solid phases separating as a eutectic mixture are magnesium and MgZn$_2$, while at E the eutectic conglomerate consists of zinc and MgZn$_2$.

The solidus comprises the two eutectic lines FG and HJ and the lines joining them to the points A, D and B corresponding to the pure metals and pure compound. The area enclosed by the dotted curve AFK shows that the solid

compound $MgZn_2$ is slightly soluble in solid magnesium, and the curve FK slopes back towards the pure magnesium axis because magnesium cannot hold so much of the compound in solid solution at low temperatures. Such a region of solid solubility is absent on the zinc side because the compound is insoluble in solid zinc.

In the experimental study of these systems much information can be obtained by reversing the usual freezing point determinations and observing the behaviour of the alloys on heating. For instance, if we heat a solid alloy of composition represented by the point a, it will remain solid until the eutectic temperature is reached ; above b the system will consist of both solid and liquid, but when the temperature is raised to c on the liquidus all the solid will be converted into liquid. Again, if we heat a solid alloy of the composition d it will remain solid until the temperature is raised to the point C when it will change completely into liquid at constant temperature. Similarly, an alloy of composition e will remain solid until the melting point of the compound is attained at D when it will melt completely at constant temperature.

The pyrometric investigations of metallic systems are made in conjunction with physical measurements by means of testing machines and the examination of the microstructure by means of the microscope. The compound $MgZn_2$, for example, has the typical microstructure of a pure metal, i.e. an aggregate of crystals of one kind. From the metallurgical point of view, however, intermetallic compounds are useless since they are brittle and mechanically weak (p. 199).

85. **Stability of the Compound.**—If the compound is not completely stable and begins to break down (dissociate) into its components in the liquid state, its freezing point will be lowered by the products of dissociation, even though neither component be present in excess. As a matter of fact, the shape of the maximum of the curve affords a rough indication of the stability of the compound as depicted in Fig. 87. The greater the stability of the compound the sharper is the maximum of the curve, and conversely, a flat maximum generally indicates considerable dissociation.

If an addition compound is perfectly stable on fusion, its freezing point will be lowered by the addition of component A or component B. The freezing point curve obtained by the addition of y moles of either component to 100 moles of the

compound AB is given by the thermodynamically derived equation

$$-\log_e\left(\frac{100}{100+y}\right)=\frac{L}{R}\left(\frac{1}{T_1}-\frac{1}{T_0}\right),$$

where L is the latent heat of fusion in calories, T_0 its absolute melting point, T_1 the absolute melting point in the presence of the excess component, and R the gas constant. By substituting various values of y we obtain the freezing point curve.

On the other hand, if the compound AB dissociates, say to the

(a) Little Dissociation   (b) Great Dissociation
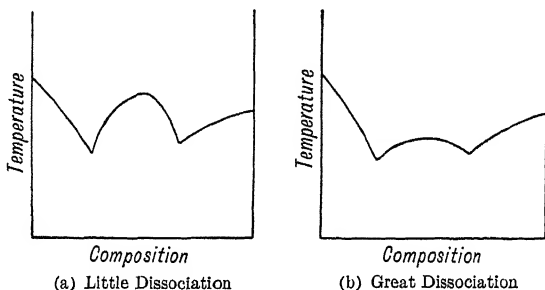
FIG. 87.   Stability of compound

extent of x per cent, the addition of y moles of the component will repress the dissociation to a smaller value x', so that

$$-\log_e\left(\frac{100-x'}{100+x'+y}\right)=\frac{L}{R}\left(\frac{1}{T_1}-\frac{1}{T_0}\right).$$

Various trial values are now assumed for x, and the curves obtained by substituting these values in the equation are compared with the actual experimental curve, until a fit is obtained.[1]

According to the law of mass action the dissociation constant K for the reaction

$$AB \;\; \rightleftarrows \;\; A + B$$
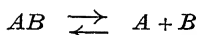
will be given by the following equations :

$$\left(\frac{x}{100+x}\right)^2 = K\left(\frac{100-x}{100+x}\right),$$

$$\frac{x'(x'+y)}{(100+x'+y)^2} = K\left(\frac{100-x'}{100+x'+y}\right).$$

The value of K can be calculated for each trial value of x, and in this way the change of x' as y is increased can be found. If the

[1] Kendall and Booge, *J. Chem. Soc.*, 1925, 127, 1768 ; Ross and Somerville, *ibid.*, 1926, 2770 ; Bennett and Wain, *ibid.*, 1936, 1114.

latent heat of fusion L is known the course of the freezing point curve can be calculated for mixtures of different composition and the value of x which gives a curve best agreeing with the experimental curve can thus be found.

86. **Type III. Formation of Compound with Meritectic or Incongruent Melting Point.**—In this type of binary system the compound which is formed suffers decomposition at a temperature below the true congruent melting point. For the general case of a solid phase S with a congruent melting point (Type II) the change of state may be represented :

$$\textit{True Melting}: \quad S \; \rightleftharpoons \; \text{liquid,}$$

while for a solid phase with an incongruent melting point (Type III) we have

$$\textit{Meritectic Reaction}: \quad S \; \rightleftharpoons \; S' + \text{liquid,}$$

where S' is a new solid phase and the liquid does not have the same composition as the parent phase.

The point A (Fig. 88) represents the melting point of one component and B that of the other component. The curve CM is the equilibrium curve for the compound formed between A and B, and the summit D of the dotted prolongation would normally be the congruent melting point of the compound. However, this point, which is called a *submerged maximum*, cannot be realised in practice, because at M the compound breaks down into another solid phase plus liquid. Since the composition of this liquid is not the same as that of the original compound the point is sometimes called an *incongruent melting point* or transition point.

The change, however, is more than mere melting and more than ordinary transition, and since it proceeds through the actual rupture of chemical links it is a true chemical reaction which is correctly expressed by a stoichiometric chemical equation. For this reason the name *meritectic reaction* will be given to this particular type of change and the temperature at which the transformation occurs will be called the *meritectic point*.[1]

---

[1] The word *meritectic* is derived from the Greek, *meros*, part, *tectic*, melting. It serves to avoid the prevalent tendency of confusing the change with the peritectic transformation of solid solutions (p. 173). In both cases we have a solid phase breaking down to a new solid phase and a liquid, but the breakdown of a solid solution is not a true chemical reaction.

A meritectic reaction will thus have the following characteristics :

(1) It may be represented symbolically :
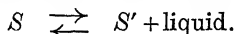
$$S \quad \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftarrows}} \quad S' + \text{liquid}.$$

(2) It takes place at constant temperature since it is accompanied by the absorption (or evolution) of latent heat of transformation.
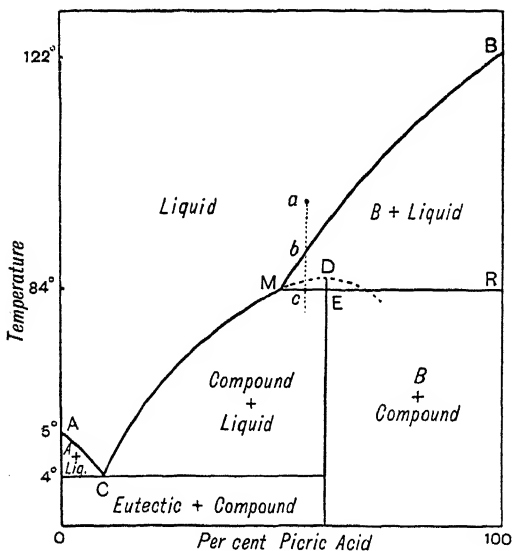
FIG. 88.   Meritectic system of Benzene and Picric Acid

(3) It is a thermodynamic or transition reaction involving lattice or morphotropic changes.

(4) It is also a true chemical reaction since it involves the rupture or formation of true chemical linkages.

(5) It can be represented by a stoichiometric chemical equation.

Benzene C_6H_6 and picric acid $C_6H_2(NO_2)_3OH$ form an addition compound $[C_6H_6.C_6H_2(NO_2)_3OH]$ which behaves in this way.   In Fig. 88 the point A is the melting point of

benzene and B that of picric acid, and the eutectic at C consists of solid benzene and the addition compound. The curve CM is the equilibrium curve for the compound with a submerged maximum at D. This point is not realised in practice because at M the compound breaks down into picric acid and liquid :

$$[C_6H_6 . C_6H_2(NO_2)_3OH] \qquad C_6H_2(NO_2)_3OH + \text{liquid}.$$
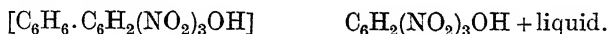
This meritectic reaction proceeds at the constant temperature of the meritectic line MER.

The essential difference between this system and one exhibiting a congruent melting point may be illustrated by considering the phenomena which occur on cooling a completely liquid system from the point a. The system preserves its liquid condition until the temperature falls to the point b on the liquidus when the pure component B crystallises out. At this stage there is no sign of the addition compound. As the temperature falls along bc, more and more of component B separates out with the result that the liquid becomes richer in component A and its composition changes along bM. When the temperature falls to c and the composition represented by the point M is reached, the addition compound makes its appearance as a new solid phase owing to the meritectic reaction

$$C_6H_2(NO_2)_3OH + \text{liquid} \qquad [C_6H_6 . C_6H_2(NO_2)_3OH].$$

Here we encounter a remarkable phenomenon, for with the further abstraction of heat the picric acid which has separated in the earlier stages begins to dissolve again to form more and more of the addition compound. This process involving the dissolution of picric acid and the formation of the addition compound takes place at constant temperature so long as any of the solid picric acid remains. After the picric acid has completely disappeared as a result of this isothermal process, further abstraction of heat from the system will now cause a fall in temperature, more and more of the addition compound separating until the normal eutectic point is reached at C. The cooling curve of this particular system is unique since it shows three thermal arrests (p. 186) corresponding to the freezing point at b, the constant meritectic temperature at c and the ordinary eutectic temperature, respectively.

Many examples of this type occur in alloy systems, for the

majority of intermetallic compounds suffer meritectic reaction of similar nature, e.g.

$$AuSn_4 \quad \rightleftarrows \quad AuSn_2 + liquid,$$
$$AuSn_2 \quad \rightleftarrows \quad AuSn + liquid.$$
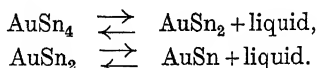
Here of course the process involves the rupture or formation of true metallic links, but may be expressed stoichiometrically as indicated in the above equations.

87. **Theory of Compound-Formation.**—The connexion between compound-formation and the type of phase diagram may be discussed from the standpoint of Kendall's theory,[1] which is illustrated diagrammatically in Fig. 89.

If the two components have absolutely no tendency to combine, the equilibrium diagram will have the simple form shown in I. In this case the solution of one component in the other obeys Raoult's law and the liquidus curves AE and BE conform to the equations for ideal solutions. Systems conforming to these conditions are rarely met with in practice.

In II there is a slight tendency towards compound-formation as indicated by the hypothetical equilibrium curve E_1ME_2. But the compound is so highly dissociated that its equilibrium curve never enters the stable region of the diagram. Although such a compound could not be detected by phase investigations, the tendency towards compound-formation is indicated by the fact that the solution of the two components does not obey the ideal solution laws, and the slope of the liquidus can no longer be calculated from the simple equations for ideal solutions.

In III compound-formation can be detected in practice since the equilibrium curve of the compound has now entered the stable region. The compound, however, has a limited stability interval extending from E_1 to P, the incongruent melting point or meritectic point. The submerged maximum M is not realisable owing to the meritectic reaction at the point P.

In IV the stability interval of the compound has expanded to such an extent that the compound now shows a congruent melting point. This point is realisable in practice because the compound is stable at its melting point. The curvature in the vicinity of this point, however, indicates that there is some dissociation into its components.

[1] *J. Amer. Chem. Soc.*, 1921, **43**, 1481.

Finally, in V the compound formed between A and B is so stable that it suffers not the slightest dissociation into its components. The sharpness of the peak at M is indicative of this great stability, and the diagram consists essentially of
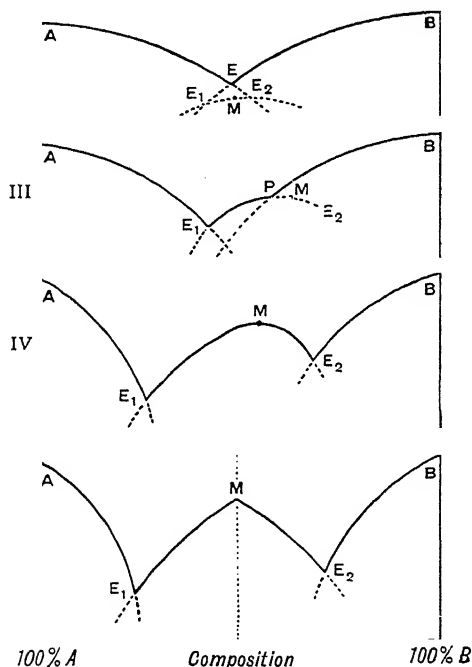
FIG. 89.   The influence of combining tendency on the type of phase diagram

two simple eutectic systems (Type I) compressed into one equilibrium diagram.

It is important to note that the liquidus departs more and more from its ideal position in I as the tendency towards compound-formation increases. In fact, the liquidus from A becomes more curved as we go from I to V because the solubility of the second component in A increases. When

both components are polar we frequently find them combining to give recognisable compounds, and the solubility of one component in the other is generally enhanced for this reason. If all solutions were ideal it would be a simple matter to calculate the solubility of a substance and the freezing points of its solutions, and to construct the equilibrium diagram from these theoretically computed data. But our solutions do not conform to the laws of ideal solutions, and each system must therefore be subjected to direct experimental investigation.

II. COMPLETELY MISCIBLE SOLID SOLUTIONS

88. The Meaning of Solid Solution.—Just as a liquid may dissolve in another liquid to give a liquid solution, so a solid may dissolve in another solid to form a solid solution. The solid crystal thus obtained is perfectly homogeneous and is sometimes called a *mixed crystal* or *isomorphous mixture*.[1] Since these terms are apt to suggest heterogeneity, it is better to employ the older term solid solution, which was used by van 't Hoff in 1890. Such a crystalline body is not a mechanical mixture of the two components, but is actually a one-phase solid solution, perfectly homogeneous like a one-phase liquid solution.

It is evident that the phenomenon is fundamentally different from the process of ordinary dissolution in a liquid, which, having no space lattice of its own, can dissolve only by destroying or breaking down the lattice of the solid. Solid solution formation involves the structural dissolution of a solid by another crystalline solid. Such a process naturally entails the spatial marshalling of the one in the other with reference to a definite space lattice.

Solid solutions are generally obtained by cooling a liquid solution of two suitable components. The preparation of such solid solutions may be illustrated by reference to the simultaneous crystallisation of potash alum, which is white, and chrome alum, which is purple. When these two salts are crystallised together from aqueous solution we obtain, not separate white and purple crystals, but one single type of

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[1] The expression *mixed crystal* is a misleading translation of the German word " *Mischkristall* " which was introduced by Roozeboom and really signifies a " Mix-crystal ". The term *isomorphous* is derived from the Greek—equal-shaped.

crystal intermediate in colour and composition between the white potash alum and the purple chrome alum. The colour and composition of the crystals will depend on the respective concentrations of the two salts in the original aqueous solution, and a whole series of solid solutions can be prepared by changing the original concentrations.

89. **Properties of Solid Solutions.**—The main facts concerning solid solutions are summarised in Retger's law which states that *the physical properties of solid solutions are continuous functions of their percentage composition.* This law, as we shall see later (p. 201), is not a completely true statement of the facts, but it does serve to express the general trend of the physical properties with the composition of the solid solution. Among the several points of interest regarding solid solutions we may note the following :

(*a*) Two substances capable of forming solid solutions will diffuse one into the other by a process of atomic or molecular migration. Thus if two metals capable of forming a solid solution are placed in contact and heated to a suitable temperature the atoms of the one metal will pass into the lattice of the other. This property of diffusion in the solid state is the basis of some important industrial processes, such as the introduction into an iron surface of zinc (sherardising), of aluminium (calorising) and of carbon (case hardening).

(*b*) The heat of solution of a mixed crystal is not equal to the sum of the heats of solution of the components as would be the case if it were merely a mechanical mixture.

(*c*) The chemical reactivity of a solid solution may be different from that of a mechanical mixture of the same components. The work of Gustav Tammann,[1] Kurt Fishbeck[2] and others has brought to light the remarkable fact that in a series of solid solutions those of certain composition are more resistant to chemical attack than the others. In the gold-silver series of solid solutions Tammann found that the alloys most resistant to chemical attack have the composition 12·5, 25, 37·5, etc., atomic per cent of gold. In the first solid solution the number of gold atoms is $\frac{1}{8}$ of the total number of atoms in the alloy, in the second $\frac{2}{8}$ and in the third $\frac{3}{8}$, and this led Tammann to suggest that the phenomenon is due to a certain symmetrical grouping in which the less noble atoms are

[1] *Zeit. Anorg. Chem.*, 1919, **107**, 1.
[2] *Zeit. Elektrochem.*, 1931, **37**, 593.

covered by the more noble atoms in the space lattice.   Obviously, factors of this kind play a fundamental part in the corrosion of alloys.[1]

In view of these findings, a solid solution may be looked upon as an intermediate stage between an ordinary physical mixture and a chemical compound.

90. **The Architecture of Solid Solutions.**—The X-ray analysis of a solid solution reveals that the " vicarious " elements replace each other atom for atom in the space lattice of the mixed crystal.   This is illustrated in Fig. 90 which shows how

	O	●	⊘
	Na	*Cl*	*Br*

Crystal of NaCl   Mixed Crystal of NaCl and NaBr
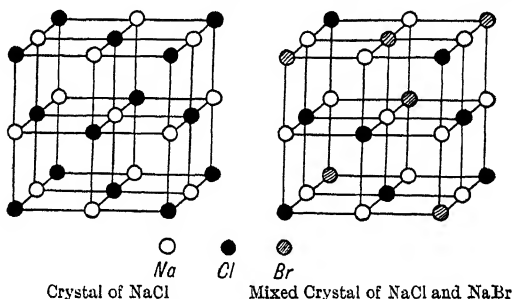
FIG. 90.   Substitutional solid solution

the bromine ions replace the chlorine ions in a solid solution of sodium chloride and sodium bromide.   There is no indication of two distinct lattices, for both components go to form the actual lattice of the solid solution.

Chiefly as a result of the work of Goldschmidt it is now established that the two chief factors contributing to isomorphism are the size and the polarisability of the ions.[2]   For two substances to be isomorphous the following conditions must be satisfied :

(1) their formulae must be analogous ;
(2) the substances must have similar unit cells containing the same number of positive and negative ions in geometrically similar positions ;

---

[1] In this connexion it may be mentioned that the most stainless Stainless Steel is obtained by a heat treatment which causes all the chromium and carbon to be retained in solid solution.   Stainless Steels contain 18 per cent Cr and 8 per cent Ni, and lose their stainless qualities if there is inter-granular precipitation of chromium or iron carbides.

[2] The polarisation describes the position of the outer electrons with reference to the atomic nuclei, while the polarisability describes the lability of these electrons when induced from their normal positions.

(3) the size of the ions must not be very different ;

(4) the polarisation of the ions must not be very different.

It is the similarity in ionic size which accounts for the unsuspected isomorphism of lead and strontium salts and of magnesium and cobalt salts. In the same way the dissimilarity in ionic size accounts for the lack of isomorphism between chemically related substances, such as the salts of sodium and potassium and those of magnesium and calcium. In general, an atom or ion can replace another without destroying the crystalline arrangement provided the ionic sizes do not differ by more than about 10 per cent. It is interesting to note that this is also the degree of disarrangement or total expansion endurable by a heated crystal before it is converted into melt. It is significant therefore that the isomorphous tolerance is the same as the thermal tolerance.

For a given structure the possibility of substitution is limited to a certain range of ion sizes and polarisabilities, and if these limits are exceeded a new space lattice is produced. To this phenomenon, involving the change-over of the space lattice as a result of substituting one ion for another, Goldschmidt has given the name *morphotropism*. According to Goldschmidt, even polymorphism (p. 48) may be regarded as a case of morphotropism, occasioned not by substitution but by thermodynamic alteration, so that the substance is no longer isomorphous with itself. It is probable that the chief factor underlying the existence of a substance in polymorphic forms is the influence of temperature on the polarisability.

Organic Compounds.—In the case of non-polar organic compounds the following conditions must generally be satisfied before two substances can form solid solutions :

(1) their chemical constitutions must be analogous ;

(2) the crystal structures must be similar ;

(3) their molecular volumes must be nearly equal.

These conditions are embodied in Garelli's rule which states that *the miscibility of solids increases as their chemical relationship becomes closer.* The following substances, for example, form completely miscible solid solutions : p-dichlorobenzene and p-dibromobenzene, naphthalene and β-naphthol, maleic anhydride and succinic anhydride, and anthracene and phenanthrene.

91. **Type I. Continuous Series of Solid Solutions.**—The

general behaviour of this type of solid solution is exemplified
by copper and nickel. These metals are chemically similar
and isomorphous, mixing together in all proportions, not only
in the liquid condition but also in the solid state. The alloys
are essentially homogeneous solid solutions and the equilibria
will be readily understood from Fig. 91.

The melting point of copper is 1084° and that of nickel
1451°. The upper curve is the liquidus or equilibrium curve
of the liquid solution, while the lower curve is the solidus or

FIG. 91.   Continuous series of solid
solutions

equilibrium curve of the
solid solution. The addi-
tion of nickel to copper
raises the freezing point,
and since the freezing
points of all mixtures lie
between 1084° and 1451°,
the liquidus is continuous.
The solidus is also con-
tinuous since the melting
points of the whole series
of solid solutions lie be-
tween the melting points
of the two components.
For each temperature be-
tween 1084° and 1451°,
there is a liquid solution
of a certain composition
in equilibrium with a solid solution of another composition.
Thus, a liquid solution of composition l is in equilibrium with
a solid solution of composition s. Any system represented
by a point in the region above the liquidus is entirely liquid,
and in the region below the solidus entirely solid. A system
represented by a point in the region between the solidus and
the liquidus, as for example the point m, is partly liquid of
the composition l and partly solid of the composition s.
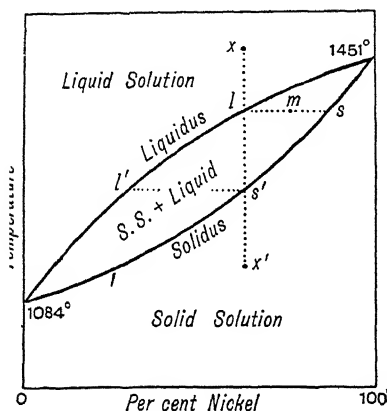
Unlike the eutectic systems these solid solutions are peculiar
inasmuch as they cannot melt or solidify at constant tempera-
ture. In the eutectic systems three phases co-exist at the
eutectic point, and this circumstance fixes the temperature,
since by the " reduced " Phase Rule F′ = 0. In the present
case, however, there are only two phases (liquid solution and
solid solution) and these are always of different composition.

Accordingly, since $F' = 1$, there is always a change of temperature during the process of fusion or solidification.

Let us now consider the changes which occur when a liquid solution represented by the point x is allowed to cool. We shall assume in all cases that the cooling is carried out very slowly so that the diffusion of the substances is complete and the solid phase always homogeneous. In other words, the operation is conducted in such a way that there is no segregation of the material. If these conditions are satisfied the system will pass along the line xx'. When the temperature falls to l a solid separates, which is neither copper nor nickel, but a solid solution of copper and nickel with a composition represented by the point s. As the temperature continues to fall, more and more solid solution will be deposited, and since the solid phase is relatively richer in nickel, it follows that the liquid phase will be progressively robbed of this constituent. The composition of the liquid solution will therefore move along the curve ll', while the composition of the solid solution will change simultaneously along the curve ss'. The composition of the solid when the last drop of liquid solidifies is represented by the point s' vertically below l, while the last drop of liquid will possess the composition represented by l'. This point also gives the final temperature of solidification.

On the other hand, if we heat a solid solution of composition x', it will begin to melt at the temperature s' with the production of a liquid of composition l'. The further application of heat will cause the temperature of the mass to rise, more of the solid will melt and the composition of the two phases will change. Finally, when the temperature reaches the value of the point l, the whole mass will have liquefied. It is clear from these considerations that the temperature of the system during the process of melting or freezing extends over the range ls'. This behaviour is characteristic of a continuous series of solid solutions.

92. **Type II. Minimum Melting Solid Solution.**—This type of binary system in which a certain solid solution possesses a lower melting point than any other solid solution of the series is fairly common. Sodium carbonate and potassium carbonate provide a system of this kind as shown in Fig. 92.

The melting points of sodium carbonate and potassium carbonate are $820°$ and $860°$ respectively, while the solid solution of minimum melting point melts at $690°$. The upper

curve is the liquidus and the lower curve the solidus and these meet at the minimum point where the compositions of the solid

FIG. 92.   Minimum melting solid solution

and liquid phases are identical. This particular solid solution will melt completely and freeze completely at constant temperature. In this respect, therefore, it simulates a pure substance or a eutectic mixture. In the case of true eutectics, however, there are two freezing point curves *intersecting* the solidus at the eutectic point, whereas with this type of solid solution there is only one continuous freezing point curve which *meets* the solidus at the minimum point.
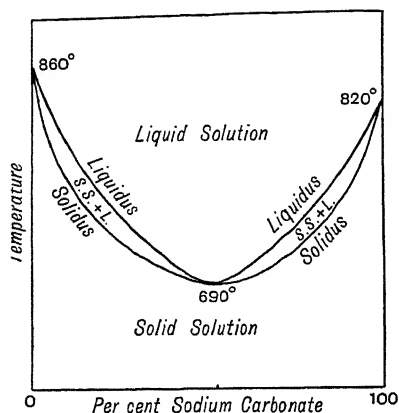
The low-melting 50 per cent mixture of the two salts is used in qualitative analysis as "fusion mixture". Advantage is also taken of this property in the production of explosive shells, since the risk of premature explosion during the filling operations is greatly minimised by the use of low-melting mixtures of explosives.

93. Type III. Maximum Melting Solid Solution.—This type of system is very rare, but this behaviour is exhibited by the optical isomers *d*-carvoxime and *l*-carvoxime ($C_{10}H_{14}N.OH$).

In Fig. 93 the upper curve is the liquidus and

FIG. 93.   Maximum melting solid solution

since it passes through a maximum it follows that the freezing point of either component is raised by the addition of
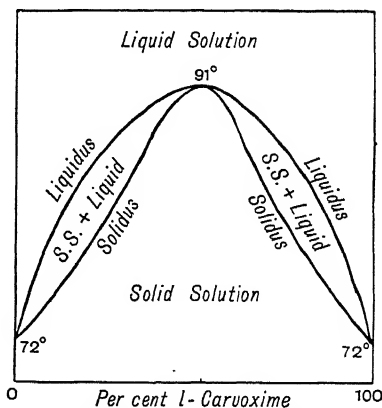
the other component. Actually, the maximum corresponds to equimolecular proportions of the two components, and the maximum freezing point (cf. maximum boiling point, p. 115) is 91°, whereas the freezing point of each component is 72°.

The lower curve is the solidus and this meets the liquidus at the maximum point where the composition of the liquid solution is the same as that of the solid solution. Consequently, this particular solid solution will simulate a pure substance inasmuch as it will melt completely and freeze completely without change of temperature.

94. Fractional Crystallisation of Solid Solutions.—The process of fractional crystallisation is analogous in some respects with the fractional distillation of liquids (p. 109). In the case of solid solutions of Type I it is possible to effect practically com-

FIG. 94. Fractional crystallisation of a solid solution

plete separation of the two components by the repeated application of the process. The theoretical basis of the method will be readily understood from Fig. 94.

Let us examine the changes which occur when a system represented by the point x is allowed to cool. When the temperature has fallen to l a solid solution of composition s will separate. Suppose now that the temperature is lowered to x' and that the deposited solid is mechanically removed from the liquid. Evidently, the solid solution thus obtained will possess the composition s'. Let us now heat this solid solution to the point x'' (where it is completely liquefied) and then allow it to cool. When it has cooled to l'' there will be separation of a solid solution of composition s'', which is much richer in component B than the original solid solution. If we repeat the process the successive crops of solid solutions will become richer in component B. Many systematic repeti-

tions of the process will ultimately lead to a practically complete separation of the two components.

As in the analogous case of the distillation of azeotropic mixtures the process of fractional crystallisation cannot be applied to· solid solutions if the freezing point curve shows a minimum or a maximum.   If the process be applied to systems of Type II or Type III we shall ultimately obtain the minimum or maximum melting solid solution as one final fraction and pure A or pure B as the other fraction according to their initial relative concentrations in the mixture.

III. PARTIALLY MISCIBLE SOLID SOLUTIONS

95. **Miscibility of Solids.**—Just as a liquid may be partially miscible with another liquid (p. 99) so a solid may be partially soluble in another solid.   Thus a solid B may dissolve in a solid A until the concentration of the resulting solid solution attains a certain definite value, say c_1. Similarly, the solid A may dissolve in component B to form a saturated solid solution of concentration c_2. The respective saturation values of the two solid solutions will be different for different temperatures
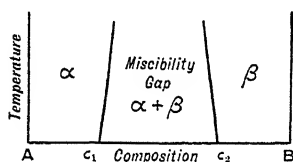
FIG. 95.   The miscibility gap

so that the phase diagram will show a miscibility gap as indicated in Fig. 95.   The miscibility gap is thus a heterogeneous region containing a mixture of the first or α-solid solution and the second or β-solid solution.   Since the solubility of a solid in another solid usually increases with temperature it is generally found that the miscibility gap becomes narrower with rising temperature.

If we apply the " reduced " Phase Rule to a two-component system consisting of α-solid solution, β-solid solution and liquid solution we find that $F'=0$.   This implies that the point at which these three phases coexist is invariant and that the temperature-concentration curves are no longer continuous but exhibit a break at this point.   Systems which behave in this way may be divided into two types according as the temperature-concentration curve exhibits a peritectic or a eutectic point.   Both types are very common, especially in alloy systems.

96. Type I. Peritectic System of Two Solid Solutions.—
The term peritectic reaction is applied to the break-down of a
solid solution (α) into another solid solution (β) plus liquid, or
conversely, to the interaction of a solid solution (β) with a
liquid to produce another solid solution (α) at constant tem-
perature. This type of transformation is of considerable
importance in metallurgy inasmuch as many well-known
alloys, such as steel, brass, amalgams, etc., exhibit phase
reactions of this kind. A peritectic reaction has the following
characteristics :
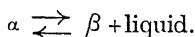
(1) It may be represented :

$$\alpha \; \overset{\longrightarrow}{\underset{\longleftarrow}{}} \; \beta + \text{liquid}.$$

(2) It takes place at constant temperature since it is
accompanied by the absorption (or evolution) of
latent heat of transformation.

(3) It is a thermodynamic or transition reaction involving
lattice or morphotropic changes.

(4) It is not a chemical reaction since it does not involve
the rupture or formation of true chemical linkages.

(5) It cannot be represented by a stoichiometric chemical
equation as may the meritectic transformation of
true chemical compounds :

$$S \; \overset{\longrightarrow}{\underset{\longleftarrow}{}} \; S' + \text{liquid}$$
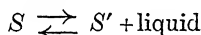
The alloys of mercury and cadmium or cadmium amalgams
may be taken as a simple example of this type. It is evident
from Fig. 96 that the addition of cadmium to mercury raises
the freezing point, while the addition of mercury to cadmium
lowers the freezing point. The curves AP and AE are the
liquidus and solidus of the first solid solution or α-phase,
while BP and BR are the corresponding liquidus and solidus
of the second solid solution or β-phase. At 182°, the tempera-
ture of the line PER, the liquid of composition P, is in
equilibrium with two solid solutions represented by E and R,
respectively. This is the temperature at which the peritectic
reaction
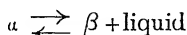
$$\alpha \; \overset{\longrightarrow}{\underset{\longleftarrow}{}} \; \beta + \text{liquid}$$

takes place.

If we cool a liquid from the point a we find that the β-solid
solution begins to separate at b on the liquidus and the

amount increases until the system becomes completely solid
at the point c.

On cooling a solution from the point m the β-phase is de-
posited at n ; as the system moves along no the β-crystals will
increase and readjust their composition along the solidus BR
while the liquid suffers a corresponding composition change
along the liquidus BP. When the system has cooled to the
point o, there will be oP parts of β-crystals in contact with
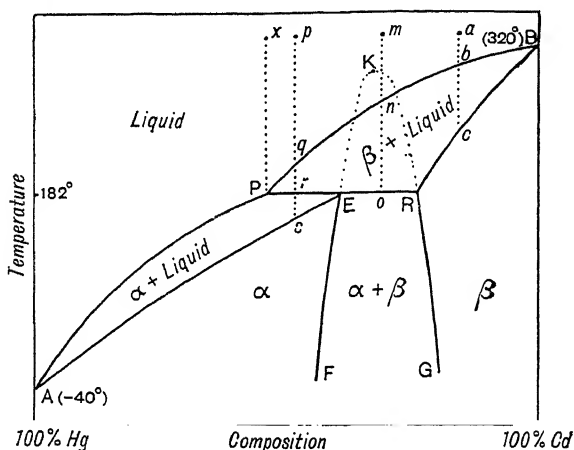
FIG. 96.   Peritectic system of two solid solutions

oR parts of liquid. If now more heat is abstracted, the
system will cool no further but preserve a constant tempera-
ture while the β-crystals and the liquid undergo peritectic
reaction to produce the α-solid solution :
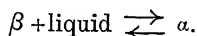
$$\beta + \text{liquid} \rightleftharpoons \alpha.$$

This reaction comes to an end when all the liquid is used up,
and the system at this stage will consist of α-phase and
β-phase. In fact, the just solidified alloy will be made up of
oR parts of α-phase (composition E) and oE parts of β-phase
(composition R). As the system of two conjugate solid solu-
tions cools down, the composition of the α-solid solution will
change along the curve EF and that of the β-solid solution
along the curve RG. These two curves define the limits of
the miscibility gap and show that the solid solubility of the

one component in the other decreases as the temperature is lowered. The theoretical prolongations of these curves meet at the hypothetical critical point K above which the two solid solutions would be completely miscible.

If we cool a liquid from the point p, the β-phase is deposited at q, and peritectic reaction sets in at the point r on the peritectic line PER. This system, however, contains more mercury than is required to transform the β-phase into α-phase, so that some liquid will remain after the completion of the peritectic reaction. Further cooling of the system will cause the residual liquid to deposit more α-crystals, until finally the whole system becomes completely solid at the point s.

A similar behaviour is observed when the original solution has the exact composition P, and is cooled from the point x, but in this case the amount of β-phase (composition R) is negligible.

97. **Type II. Eutectic System of Two Solid Solutions.**—In view of the common occurrence of this type in organic, inorganic and metallic systems, we shall consider the following representative examples.

(a) *Potassium Nitrate and Thallium Nitrate.*—As may be seen from Fig. 97 the freezing point of either component is lowered by the addition of the other component, but ultimately a point C is reached where the liquid deposits a eutectic conglomerate of two solid solutions. At this point the liquid is in equilibrium with two different solid solutions, the composition of the first being represented by D and that of the second by E.

The curve ACB is the liquidus and $ADEB$ is the solidus, while the lines DF and EG show how the concentration of the first or α-solid solution and the second or β-solid solution change as the temperature of the solid system is lowered. The area $FDEG$ is the miscibility gap within which we have a heterogeneous mixture of the two solid solutions. The theoretical analogy with the critical solution systems (p. 100) is brought into prominence by prolonging these two curves to the hypothetical critical solution point K at which the two solid solutions would be completely miscible. This point, however, is not attainable under ordinary conditions.

Mixtures containing a smaller proportion of thallium nitrate than D or a greater proportion than E produce no

eutectic and merely form one solid solution, but all mixtures between D and E will contain some of the eutectic. If we cool a mixture having the exact composition of the point C it will solidify completely as a conglomerate of the α- and β-solid solutions of composition D and E, respectively. Applying the " reduced " Phase Rule to this system we have two separate solid phases in equilibrium with one liquid so that on substituting in the equation, we have

$$P + F' = C + 1$$
$$3 + F' = 2 + 1,$$
$$F' = 0$$

and the system will therefore solidify completely at one constant temperature.

(b) *Tin and Lead.*— The equilibrium diagram for tin and lead alloys, which comprise the well-known " solders ", is shown in Fig. 98. Pure tin melts at 232° and pure lead at 327°, and the liquidus curves AC and BC intersect at the eutectic point C.
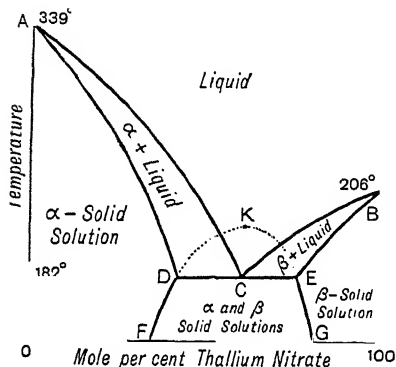
FIG. 97.   Potassium Nitrate and Thallium Nitrate giving eutectic of two solid solutions

The eutectic mixture contains 34 per cent lead and 66 per cent tin and solidifies sharply at 183°. Owing to the solid solubility of the components, the eutectic mixture is not a mixture of the separate metals but a conglomerate of two solid solutions. One is a solid solution of lead in tin with composition D and is termed the α-solid solution, and the other is a solid solution of tin in lead with composition E and is designated the β-solid solution. The lines of solid solubility DF and EG show how the composition of each solid solution changes with temperature. Thus, at 100° the composition of the α-solid solution has changed to that represented by the point F and that of the β-solid solution to that represented by G.

If we cool a molten alloy from the point x, the first solid which separates when the temperature has fallen to l is the

β-solid solution of composition s. As the β-phase separates out, the liquid becomes richer in tin, and at 235° the composition of the liquid is given by l' and that of the solid being deposited by s'. In fact, the composition of the liquid will change along BC and that of the solid along BE. Both liquid solution and solid solution readjust their compositions as the temperature falls. At 183° the solid has the composition E and the liquid the composition C. The liquid now freezes
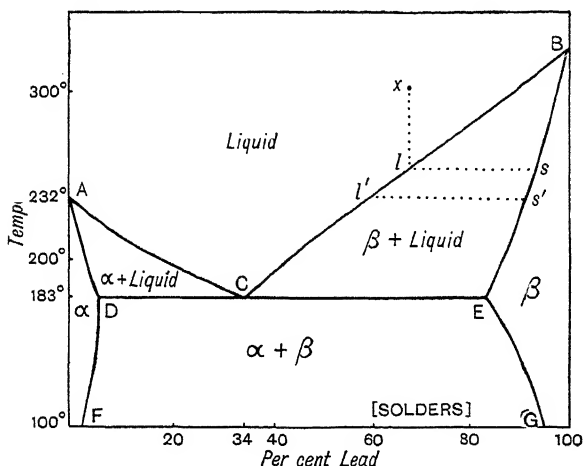
FIG. 98.   The alloys of Tin and Lead (solders)

at constant temperature to give the eutectic (α-solid solution/β-solid solution) and the proportions of these phases is given by $CE : CD$. As the temperature falls below 183°, the β-solid solution can no longer retain in solution all the tin which it contains, and so it begins to disgorge some of this metal by partly changing into α-solid solution. Thus at 100° it has broken up into α-phase of composition F and β-phase of composition G in a definite ratio. The solid obtained on reaching room temperature will therefore consist of the α/β eutectic plus a further amount of the α-phase produced through the partial breaking up of the β-phase.

The Principles of Plumbing.—From the practical point of view the tin-lead alloys are important because (*a*) they readily adhere to the clean surfaces of other metals, and (*b*) they

solidify gradually and pass through a plastic or pasty condition.

The Romans were responsible for the introduction of soldering and made extensive use of the first property. To make a solder joint, the oxide film on the surface of the metal must first be removed or dissolved by means of a flux, such as zinc chloride, ammonium chloride or resin. The primary function of the flux is to ensure intimate adhesion between the metal and the solder.

The Romans, however, did not make use of the second property, for they were not familiar with the production of a " wiped joint " in lead piping. As may be seen from Fig. 98, a solder containing 60-80 per cent of lead will have a wide pasty range between liquidus and solidus. The proportion of solid to liquid gives a good consistency for making " wiped joints " while the extent of the freezing range allows sufficient time for the operation.

(c) *Oxygen and Nitrogen. Solid Air.*—As to the nature of solid air it is interesting to enquire whether it is simply a eutectic mixture of O_2 crystals and N_2 crystals, or a solid solution of O_2 in N_2. Actually, the phase diagram is very similar to Fig. 98. Solid O_2 melts at $54°$ T and solid N_2 at $63°$ T, and the elements are partially miscible in the solid state. The α-solid solution (16 per cent N_2 dissolved in the O_2 lattice) and the β-solid solution (70 per cent O_2 in the N_2 lattice) separate as a eutectic at $50°$ T. If we solidify ordinary air, free from A, CO_2 etc., we obtain the β-solid solution, and this, when heated, begins to melt at $56°$ T and becomes clear liquid air at $60°$ T.

Incidentally, we may mention that solid oxygen exists in three crystalline or allotropic modifications. The α-form changes to the β at $23·5°$ T, and the β to the γ-modification at $44°$ T.

98. **Miscibility Gap and Type of Diagram.**—In the case of solid solutions the type of phase diagram is largely determined by the position of the miscibility gap with reference to the solidus and liquidus curves. If there is no miscibility gap or if the gap lies below the solidus curve, it is clear that the system must be completely miscible and that the liquidus and solidus curves must preserve a continuous character.

In Fig. 99 (a) the miscibility gap lies below the solidus and the system is completely miscible in the region of the solidus.

In Fig. 99 (b) the miscibility gap has expanded into the higher regions and the system now exhibits partial miscibility since the solidus is no longer continuous. In this case we have two solid solutions undergoing transition or peritectic reaction
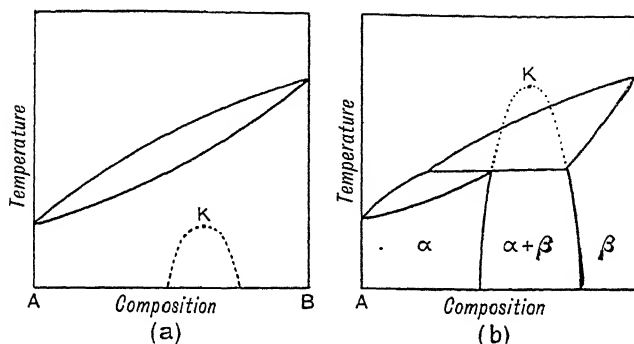
FIG.　Genesis of the peritectic type of system

as described under Type I. Although complete miscibility would be attained at the hypothetical critical point K this point is not realisable in practice.

The genesis of conditions leading to the production of a
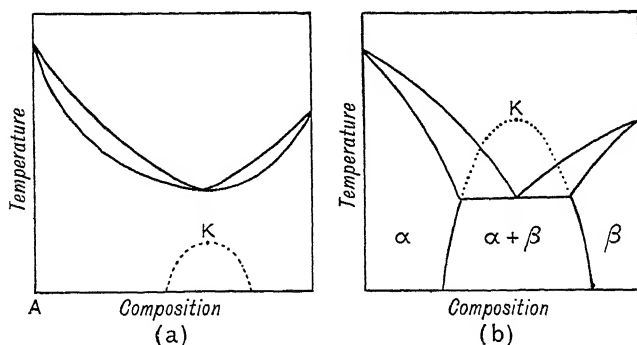
FIG. 100.　Genesis of the eutectic type of system

eutectic system of two solid solutions is illustrated in Fig. 100. These systems are derived from the minimum melting completely miscible type (Class I, Type II) through the expansion of the miscibility gap shown in Fig. 100 (a) to that

System	Curves	Characteristic	Example
CLASS I. Type I (a)		Simple eutectic	Gold and thallium
Type I (b)		Monotectic. Liquidus rising from m.p. of tin, while solidus is horizontal	Tin and silicon
Type II		Compound with congruent m.p. $S \rightleftarrows$ liquid	Benzophenone and diphenylamine. Magnesium and zinc
Type III		Compound with incongruent m.p. (meritectic). $S \rightleftarrows S' +$ liquid True chemical change	Benzene and picric acid. Certain intermetallic compounds
CLASS II. Type I		Solid solution—no maximum or minimum. Cannot melt or freeze at constant temperature	Copper and nickel
Type II		Solid solution with minimum m.p.	Sodium carbonate and potassium carbonate. (Fusion mixture)
Type III		Solid solution with maximum m.p. Very rare type	d-and l-Carvoximes
CLASS III. Type I		Partially miscible solid solutions with peritectic point $\alpha \rightleftarrows \beta +$ liquid Not expressible by chemical equation	Mercury and cadmium
Type II		Two solid solutions with eutectic point	Potassium nitrate and thallium nitrate. Tin and lead (solder)

180

shown in Fig. 100 (*b*). The gap meets the solidus at two points representing the composition of the α-solid solution and the β-solid solution at the eutectic temperature. Here again the hypothetical critical point *K* cannot be realised under ordinary experimental conditions.

A third possible type of system arising from the intersection of a miscibility gap with a maximum melting solidus curve (Class I, Type III) has never been met with in practice.

QUESTIONS

1. How would you distinguish between (*a*) a pure liquid and a constant boiling mixture, (*b*) a pure and impure specimen of a crystalline solid?   (Cambridge Higher School Certificate.)

2. Explain the terms (*a*) two-component system, (*b*) invariant system, (*c*) transition point, (*d*) metastable system, (*e*) eutectic point. Illustrate your explanation by examples.

(B.Sc., London.)

3. Write short notes on the following, giving examples in each case : (*a*) triple point, (*b*) transition temperature, (*c*) eutectic point, (*d*) consolute temperature.   (B.Sc., Manchester.)

4. Discuss the various types of melting point curve obtained from mixtures of two substances. What is meant by the eutectic point of a mixture ? What kind of substances form eutectics ?

(B.Sc., Sydney.)

5. Describe the phenomena of the eutectic crystallisation of a binary system. What would be the general character of the freezing point curve for mixtures of two metals which enter into chemical combination ? Which mixtures of the two metals would solidify completely at one temperature ?   (B.Sc., London.)

6. The freezing points of molten mixtures of two substances *A* and *B* are as follows :

Atom % of *B* .	0	10	20	30	40	50	60	70	80	90	100
Temperature .	65°	60°	50°	35°	50°	55°	50°	35°	20°	30°	35°

Draw and interpret the freezing point curve, and explain what happens when molten mixtures containing 20, 30 and 70 atoms per cent of *B* are cooled down.   (B.Sc., St. Andrews.)

7. Mixtures of two components, *A* and *B*, on being cooled, gave the following results in a series of temperature-time experiments : line *N* gives the number of the experiment, *x* the per-

centage of B in the mixture, T the first arrest point and T' the
second arrest point :

N	.	1	2	3	4	5	6	7	8	9	10
x	.	0	18	23	29	33	44	55	65	82	100
T	.	1530°	1303°	1312°	1435	1443°	1426°	1322°	1322°	1398°	1420°
T'	.	None	1262°	1262°	1262	None	1270°	1270°	1270°	1270°	None

Draw the equilibrium diagram and comment on its form.

(Sub. B.Sc., Wales.)

8. Draw an approximate Phase Rule diagram for the antimony-
bismuth system from the following data :

Melting point of Bi	268°
Melting point of Sb	632°

The two metals are completely miscible in the fused state and
form solid solutions in all proportions.   No compounds are formed.

By reference to your diagram describe what happens when a
molten mixture containing 50 per cent antimony is cooled slowly
from 600° to 200°.   (B.Sc., Leeds.)

9. When alloys of thallium and mercury containing Pg. of
thallium per 100 g. mixture are cooled, they begin to solidify at
the temperature T and become completely solid at the tempera-
ture t.

P	$T°$	$t°$	P	$T°$	$t°$
0	-39	-39	35	9	0
5	-49	-59	40	0	0
9·3	-59	-59	60	122	0
15	-8	-59	80	212	0
20	-8	-59	85	235	35
27	13	-59	92	267	148
30	14	0	100	303	303

Plot the figures on graph paper, and interpret the
diagram.   (Hg $= 200·6$; Tl $= 204·4$.)   (B.

10. What is a solid solution ? Give an account of the different
types of phase diagrams which may occur in binary systems
forming solid solutions. What factors usually determine the
formation of mixed crystals ?   (M.A., Edinburgh.)

11. Draw the freezing point diagrams for the five principal
cases of a system composed of two solids which form solid
solutions, and indicate on the diagrams the nature of the various
phases present.   (B.Sc., Special, London.)

12. Enumerate the chief kinds of freezing point diagrams for
two-component systems and discuss one of them with the aid of
the Phase Rule.   (B.Sc., Sheffield.)

13. Sketch an equilibrium diagram in which a peritectic reaction is represented. Describe with reference to the diagram, the nature of the peritectic reaction. (B.Sc., Birmingham.)

14. How may the Phase Rule be applied to disclose the existence and composition of compounds ? Illustrate your answer by reference to (a) hydrate formation, (b) alloys, (c) the system AgCl-NH$_3$. (M.A., Edinburgh.)

THERMAL ANALYSIS AND ITS APPLICATIONS

Only a signal shown and a distant voice in the darkness.—LONGFELLOW

99. **Cooling Curves and Arrests.**—The practical determination of equilibrium curves is usually carried out by taking the cooling curves of mixtures of various compositions and ascertaining therefrom the initial and the final solidification temperatures. These data enable us to draw the liquidus and solidus curves of the equilibrium diagram.

When the temperatures concerned are not excessive, ordinary thermometers may be employed for recording the temperature of the system, but in the case of metallic and high-melting systems generally, thermocouples are invariably used for this purpose. This method based on the study of cooling or heating curves is called *thermal analysis.* Essentially, the method depends on the fact that the occurrence of any phase reaction involving the appearance or disappearance of a phase is always accompanied by a heat effect which is duly registered on the cooling curve.

When a pure (one-component) substance is allowed to cool slowly and its temperature recorded at definite intervals of time, the rate of cooling can be represented by means of a cooling curve as shown by *ab* in Fig. 101. When the freezing point is reached (super-cooling assumed to be absent) the liquid will begin to solidify and the temperature will now remain constant until all the liquid is converted into solid, as indicated by the horizontal line *bc*. Finally, with the further cooling of the solid phase, there will be a regular fall of temperature as indicated by *cd*.

On the other hand, when a solution or a liquid system of two components is allowed to cool slowly, the cooling curve will be of the form shown in Fig. 102, except for the special cases to be mentioned later. The line *ab* represents the cooling

of the fused mass before the incidence of freezing. At b one of the components begins to crystallise out and during this stage the mixture does not cool so rapidly since the process is attended by the evolution of heat. With the appearance of the solid phase the curve exhibits a break at b and this is called the first " arrest point " or " arrest ".

As more and more of the solid separates, the composition of the solution changes, so that the temperature of equilibrium does not remain constant but continues to fall along bc. At c, both components crystallise out as a eutectic mixture and the liquid now solidifies as a whole at constant temperature.
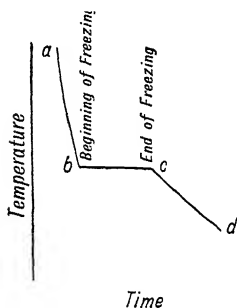
FIG. 101.   Cooling curve of pure
substance (one component)
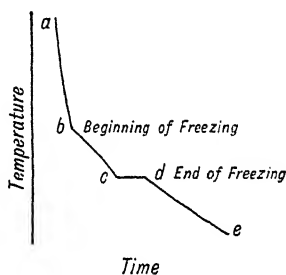
FIG. 102.   Cooling curve of
solution (two components)

This point is the second arrest. After the complete solidification of the mixture the system cools down steadily until the ordinary temperature is reached, and no further arrest occurs unless the solid material suffers some kind of allotropic or phase reaction. In actual practice, the breaks in the curve may not be sharp owing to irregular cooling and supercooling effects, but even in these cases the temperatures corresponding to the arrests may be determined with a high degree of accuracy.

100. Construction of Equilibrium Diagram.—By applying the above procedure to several mixtures of different composition[1] we obtain a series of cooling curves which may be used to construct the complete equilibrium diagram. The upper diagram in Fig. 103 represents a series of cooling

[1] The total weight of mixture taken for examination should be roughly the same in each case in order to preserve comparable rates of cooling and to facilitate the exploration of the eutectic region.

curves obtained with various mixtures of two components A and B. The first curve refers to a system containing $100\%A + 0\%B$, and the other curves to mixtures containing $80\%A + 20\%B$, $60\%A + 40\%B$, $40\%A + 60\%B$, $20\%A + 80\%B$, while the extreme curve is the cooling curve for the system
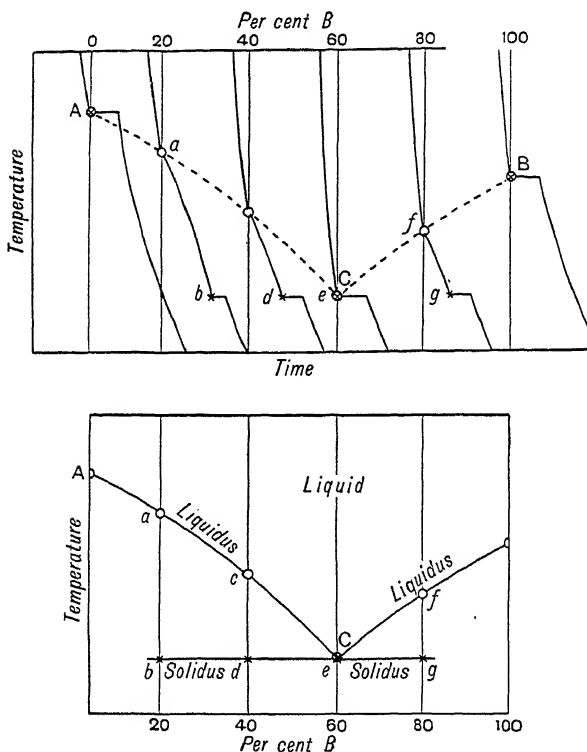
FIG. 103. Construction of equilibrium diagram from cooling curves

$0\%A + 100\%B$. By joining the points of first arrest (represented by circles) we obtain the liquidus curves, while the solidus is obtained similarly by drawing a line through the second arrest points (represented by crosses). Actually, of course, it is only necessary to plot the arrest temperatures on graph paper as indicated in the lower diagram. It is clear that this particular system forms a eutectic containing 60 per cent of B.

With regard to the cooling curves themselves it will be noticed that the horizontal part corresponding to the separation of the eutectic increases to reach a maximum at the exact eutectic composition, and then decreases. If the mixture under investigation has the exact eutectic composition it
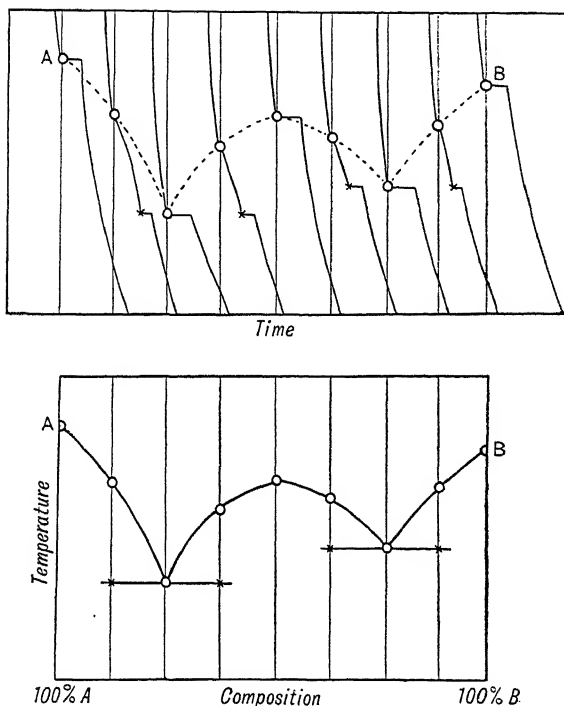
FIG. 104.   Cooling curves and diagram showing compound formation

freezes as a whole at constant temperature and the cooling curve shows one arrest only.

Compound Formation.—If a compound is formed the cooling curves for the various mixtures will have the general form shown in Fig. 104. The systems corresponding to pure *A*, pure *B*, pure compound *A-B*, first eutectic mixture and second eutectic mixture will each show but one protracted arrest. All other mixtures will give cooling curves with two arrests, the first corresponding to the initial crystallisation

temperature and the second, more protracted arrest to the final solidification or eutectic temperature. As indicated above the plot of the points of first arrest gives the liquidus, and those of the second arrest the solidus of the equilibrium diagram.[1]

Solid Solution.—In the case of substances which are able to form a continuous series of solid solutions, each pure
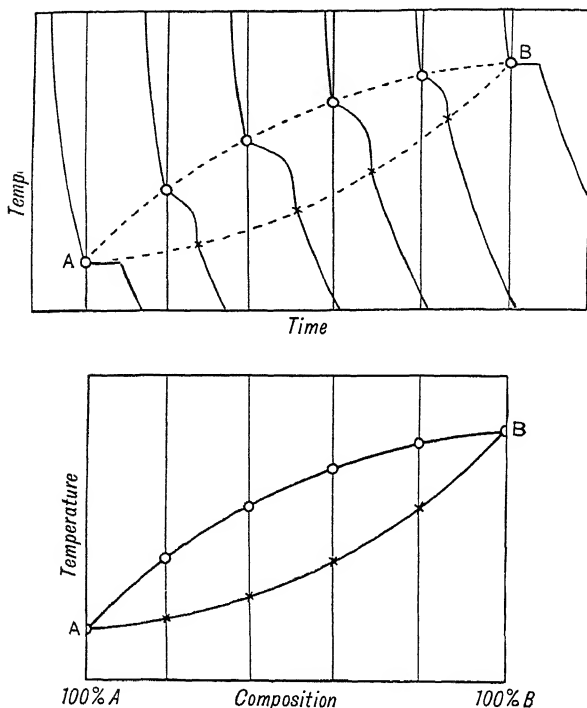
FIG. 105.   Cooling curves and diagram for solid solution

component will naturally give the ordinary type of cooling curve showing a protracted arrest (horizontal line) at the freezing point (Fig. 105). The cooling curves of all mixtures, however, will show two arrests; the first (represented by a circle) corresponds to the liquidus or beginning of freezing,

[1] If the compound has a meritectic or incongruent melting point, the cooling curve of the system may show *three* arrests, as described on p. 161.

and the second (represented by a cross) to the solidus or end of freezing. The cooling curves of solid solutions of this kind differ from the preceding types inasmuch as they do not show a protracted arrest or horizontal portion characteristic of eutectic systems. In fact, the cooling curves for these solid solutions show mere breaks, but it is only necessary to plot the temperatures corresponding to these breaks in order to obtain the liquidus and solidus curves shown in the lower diagram.

Owing to the slowness with which the separated solid phase readjusts its composition in order to come to equilibrium with the liquid mixture, it is much better to investigate these systems by the heating method. For this purpose the solid system

(a)   Ordinary cooling curve   (b)   "Inverse rate" curve

FIG. 106.   Methods of plotting cooling curves

is slowly heated, and the points of incipient fusion and complete liquefaction found from the heating curve or directly observed by the eye (p. 209).

Allotropic Transformations.—For investigating solid-solid transformations in alloys and similar materials in which the heat effect is less pronounced, the cooling curve may be plotted as an "inverse rate" curve in order to bring out more clearly the point at which the exothermic or endothermic phase reaction occurs.

The method is illustrated in Fig. 106. In the ordinary method we plot the temperature θ against the time t, but by plotting $\dfrac{dt}{d\theta}$ against t we obtain the "inverse rate" curve in which the heat effect accompanying the phase change is prominent as a peak on the curve.

I. THE BEHAVIOUR OF OPTICAL ISOMERS

101. **Types of Diagrams.**—When two optical antipodes crystallise in equimolecular proportions the deposited material may be

(a) a eutectic or d/l mixture of the separate d- and l-forms ;

(b) a true double salt or racemic compound formed by the chemical combination of the d- and l-forms ;

(c) a solid solution formed by the mutual dissolution of the d- and l-forms in the solid state.

In the first case the equilibrium diagram will be of the simple eutectic type shown in Fig. 107. Since the melting points of the two components are practically identical, the freezing point curve will be symmetrical. An example of such a system is provided by d-pinene ($-63°$) and l-pinene ($-63°$) which give a 50-50 eutectic at $-120°$.
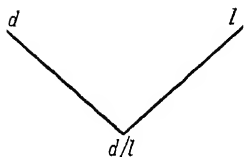
Per cent l–Pinene

FIG. 107. Mechanical mixture of d- and l-forms

In the second case, a system in which a true racemic or r-compound is formed will have one or other of the equilibrium diagrams shown in Figs. 108 and 109. There will now be three distinct freezing point curves corresponding to the three phases —d-form, r-compound and l-form. Since the melting points of the d- and l-forms are practically the same, the curves will be symmetrical, but the melting point of the compound

O   Per cent l–Dimethyl Tartrate   100
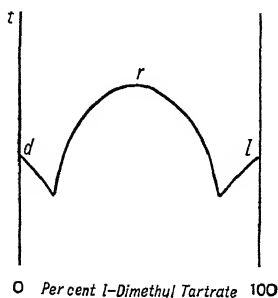
FIG. 108. Formation of r-compound with higher melting point

O   Per cent l–Mandelic Acid   100
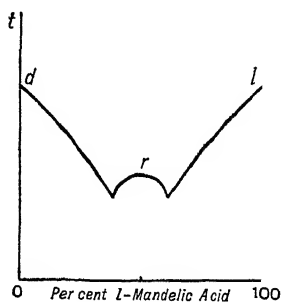
FIG. 109. Formation of r-compound with lower melting point

may be above or below that of the antipodes. Thus r-dimethyl tartrate melts at $89°$ while the d- and l-forms melt

at 43° (Fig. 108).   On the other hand, r-mandelic acid melts
at 118° while the optical antipodes melt at 133° (Fig. 109).[1]

In the third case the d- and l-forms dissolve in each other
to form a solid solution and the freezing point curve may
assume one of the three forms for completely miscible solid
solutions (p. 180).   Actually, however, only two of these types
have been observed in practice.   In the first (Fig. 110) the
freezing point curve is simply a straight line lying horizontally
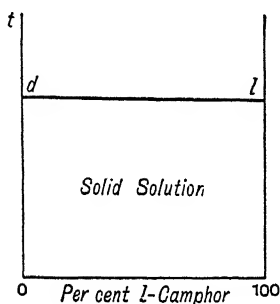
FIG. 110.   Solid solutions with
same melting point
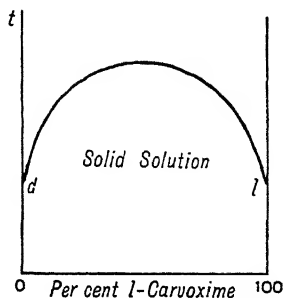
FIG. 111.   Solid solution with
higher melting point

across the diagram since the whole series of solid solutions have
the same melting point.   A straight line of this kind is given
by mixtures of d- and l-camphor.

In the second type (Fig. 111) the freezing point curve shows
a maximum.   This behaviour is exhibited by d- and l-carvoxime
as described previously (p. 170).

102. **Tests for d/l-Mixtures, r-Compounds and Solid Solu-
tions.**—It is easy to see from the above diagrams that the
behaviour of a given optically inactive crystalline material on
the addition of either the d- or the l-form will be different
according as the substance is a d/l-mixture, an r-compound or
a solid solution.

[1] The supposed identity of the d- and l-forms is really an unproved
assumption.   Campbell and Garrow (*Trans. Faraday Soc.*, 1930, **26**.
560) found that the melting point of d-mandelic acid is 132·75° and
l-mandelic acid 132·90°.   The solubilities are also different : 100g.
water dissolves 11·36g. d-mandelic acid but only 10·98g. l-mandelic
acid.   According to the theory of wave mechanics the d- and l-forms
of a compound must differ slightly in energy and rotatory power.   In
the cases studied up to the present, however, the Raman spectra are
found to be identical.

In order to decide the nature of the substance, we need only take its melting point, add a little of the *d*- or the *l*-form and then take the melting point of the mixture. By adding successive quantities of the optically active form and finding the melting points of these mixtures, we obtain a melting point curve. If this curve rises to the melting point of the separate forms, the original substance is simply a mechanical mixture of the *d*- and *l*-forms (Fig. 107). On the other hand, if the curve falls and then rises, the substance is a true racemic compound (Figs. 108 and 109). Finally, if the curve is a straight horizontal line (Fig. 110) or if the curve falls off continuously to the melting of the separate forms, the original material is a solid solution of the optical antipodes.

Incidentally, the most convenient way of distinguishing between a *d/l*-mixture and a racemic compound is to examine the optical rotation of a saturated solution of the material after adding excess of one isomer. If the solution is saturated with the *d*-form and the *l*-form, then the addition of either modification will produce no optical activity in the solution, because it does not dissolve. On the other hand, if the solution is saturated with the *r*-compound (which is a distinct solid phase differing from the *d*- and *l*-phases), it can still dissolve the *d*-form or the *l*-form and thus become optically active.

II. IRON AND STEEL

Gold is for the mistress, silver for the maid,
Copper for the craftsman, cunning at his trade ;
" Good ! " said the Baron, sitting in his hall,
" But iron ! cold iron ! is the master of them all."—KIPLING

103. **The Different Varieties of Iron.**—In view of the great industrial importance and manifold uses of steel in the present age it is desirable that the student should be familiar with salient features of the phase reactions which occur in this remarkable material.

Pure iron can exist in three definite allotropic modifications which are designated α-iron, γ-iron and δ-iron, respectively. The existence of these varieties is betrayed by the arrests on the cooling curve, since there is always a heat effect when one modification is transformed into the other.

When molten iron is cooled, it solidifies at 1537° and the

solid produced is δ-iron with a body-centred cubic lattice. When the temperature is lowered further, the cooling curve (Fig. 112) shows an arrest at 1400° owing to the transformation of the δ-iron into γ-iron which possesses a face-centred cubic lattice. During the further cooling, this lattice is preserved until at 900° the γ-iron changes into α-iron which has a body-centred cubic lattice. The ordinary form of iron which is stable at room temperature is α-iron. The above changes are reversed on heating, the α-iron changing into γ-iron and this again into δ-iron as the temperature is raised. The temperatures at which these changes occur are really transition points, but the metallurgist, faithful to his own terminology, calls them " critical points " and labels them Ar_3 and Ar_4, and refers to the different varieties of iron as α-ferrite, γ-ferrite and δ-ferrite, respectively. The chief properties of the three varieties of iron are given in the table below.

Fig. 112.   Transformation points of iron

The precise significance of the short arrest at 769° is by no means clear, but the change can hardly be regarded as an actual phase transformation since the space lattice is the same above and below this temperature. The point appears to be intimately connected with the production

THE ALLOTROPIC FORMS OF IRON

Property	α-Iron	γ-Iron	δ-Iron
Thermal range .	Up to 906°	906-1404°	1404-1537°
Space lattice .	Body-centred cube	Face-centred cube	Body-centred cube
Hardness . .	Soft	Hard	..
Magnetic character	Strongly magnetic	Non-magnetic	Non-magnetic
Solubility of carbon in	Insoluble	Readily soluble	Soluble

of magnetic properties in the metal, but as we are primarily concerned with actual phase reactions only, we give no further consideration to this singular property of the system.

104. The Iron-Carbon System.—A system consisting of iron and carbon may give rise to several solid phases which enter

into various equilibria with one another according to the conditions. The solid phases which may occur in these circumstances comprise

> One of the three forms of iron
> Carbon
> Solid solution of carbon in γ-iron called *Austenite*
> Iron carbide, Fe_3C, called *Cementite*
> Solid solution of carbon in δ-iron

The Constitutional Diagram.—The constitutional diagram of the iron-carbon alloys is singularly restricted in its concentration range. The so-called complete diagram does not extend beyond a carbon concentration of 6 per cent, because the rapid rise of the liquidus beyond this limit renders thermal measurements difficult and of doubtful accuracy. The steels include alloys containing up to 1·7 per cent of carbon while the cast irons contain from 2·2 to 6·6 per cent of carbon.

In Fig. 113 the area AGE is the region of stability of δ-iron; the area ABE is the region in which δ-iron solid solutions and corresponding molten mixtures are in equilibrium; the area GEF is the region in which δ-iron solid solution is in equilibrium with γ-iron solid solution, and the line EFB represents the peritectic transformation
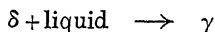
$$\delta + \text{liquid} \;\longrightarrow\; \gamma$$

at constant temperature. The curve AB is the liquidus for solutions in δ-iron; when a molten mixture is cooled to a point on the liquidus it will deposit, not iron, but the δ-solid solution (since iron in the δ-condition is able to dissolve carbon).

The curve BC is the liquidus for solutions of carbon in γ-iron; when a molten steel within this range is cooled to a point on the liquidus the solid deposited is not iron but the solid solution *austenite* (since iron in the γ-condition is also able to dissolve carbon). The curve CD is the liquidus for solutions of iron carbide, and when a system in this region is cooled to a point on the liquidus there is separation of Fe_3C or *cementite*. At the eutectic point C the eutectic conglomerate of austenite and cementite separates at constant temperature. This eutectic corresponds to a temperature 1130° and a composition 4·3 per cent of carbon.

The solidus curves comprise AE, EF, FH, HC and CP.

As we have already noted, γ-iron is capable of holding carbon in solid solution to give austenite, which occupies the region *GFHKM*.

Changes after Solidification.—Although carbon may be in perfect solution after solidification of the alloy, it may be given up again or precipitated when the steel is cooled down.
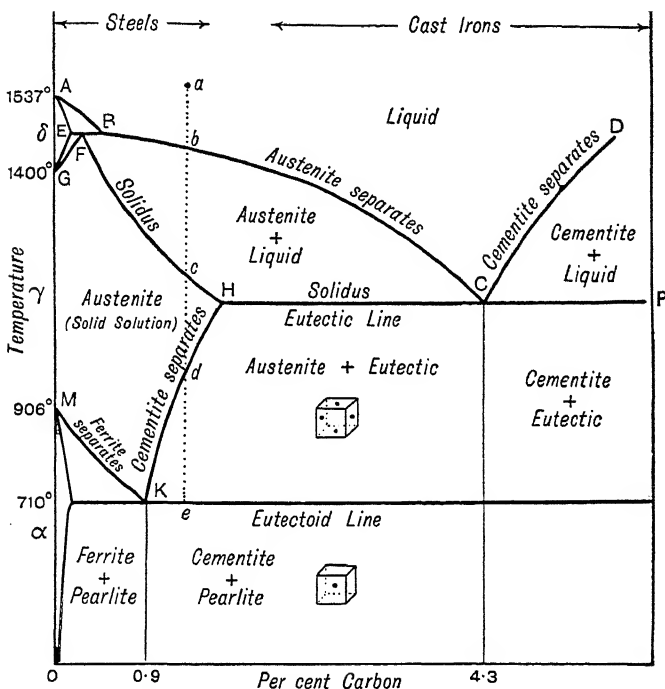
FIG. 113.   The constitutional diagram of Iron-Carbon alloys

When a saturated austenitic steel is cooled, it throws out of solution some of its carbon in the form of Fe₃C. This occurs along the curve *HK*. On the other side we have the transition curve *MK* along which the austenite changes into α-iron. The two curves intersect at the point *K* which thus defines the lower limit of true stability of the austenitic solid solution. When an alloy of carbon content less than 0·9 per cent is cooled to this temperature, it changes from a homogeneous solid solution into a mixture of α-iron and Fe₃C (cementite),

which is termed a *eutectoid*.[1]   Owing to its pearly lustre under the microscope this eutectoid is called *pearlite*.

Let us now examine the phase reactions which occur when a molten steel is cooled from the point *a*.   When the temperature falls to *b*, austenite containing about 0·4 per cent of carbon is deposited from the solution.   As the temperature continues to fall, these crystals not only increase in size but take up carbon from the molten liquid so that their composition changes along the line *FH*, and when the point *c* is reached the whole system solidifies to solid austenite.   This solid solution cools without further change until the point *d* is reached, where the γ-iron changes to α-iron.   Since α-iron is not capable of dissolving carbon or carbide, the phase reaction

Solid Solution (austenite) Fe_3C (cementite)

takes place because the solid solution cannot hold all its carbon at these lower temperatures.   Accordingly, the carbon content of the residual solid solution decreases along the line *HK* until at the temperature and concentration given by *e* the system breaks down into pearlite and cementite.   On the other hand, if we slowly cool an alloy containing less than 0·9 per cent carbon the steel will consist finally of a mixture of α-iron and pearlite.

The nature of the final alloy will be quite different if the cooling is rapid, since this does not permit true equilibration of the system.   Rapid cooling does not give time for the solid solution to change into cementite as indicated in the above equation, and the result is a hard steel.   The character of the steel is intimately connected with the degree of break-down of the austenite into cementite and pearlite, and this in turn depends upon the particular thermal treatment to which the material has been subjected.

105. **Heat Treatment of Steel.**—The heat treatment of alloys has for its object the alteration of the character of the metal

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[1] The term *eutectoid* is applied to the intimate mixture of two solid phases which is produced at constant temperature on cooling a solid solution :

Solid Solution I $\longrightarrow$ Solid II   +   Solid III ;
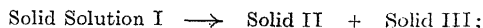
eutectoid

cf.   Liquid Solution I   Solid II   +   Solid III

eutectic

so that it acquires certain desirable physical characteristics. In the case of steel such treatment generally involves the heating and the cooling of the material under regulated conditions, so that the degree of break-down of the austenite may be controlled and brought to a desired value. According to the particular degree of resolution and the nature of the subsequent treatment, there is produced *martensite, troostite, sorbite* or *pearlite* or aggregates of these constituents.

The process of *annealing* is applied for the purpose of removing the hardening effects which are invariably produced by cold work on the metal. The metal is raised to a temperature beyond the critical range and is then allowed to cool slowly in order to promote a pearlitic and fine-grained structure. This process releases the internal strains and renders the metal softer and more ductile. *Normalising* is a similar process in which the steel is heated to the annealing range and then cooled in the air so that the material acquires a uniform structure. The *hardening* of steel, on the contrary, is effected by heating the metal above the critical temperature (usually bright redness) and cooling it rapidly by quenching in a cold liquid.

If a steel article is heated below red heat the hardness is partially removed and the material recovers some of its elasticity. This process is called *tempering*. When the article is heated slowly in the air, the surface layer assumes various tints from straw (220°) to violet (295°) according to the temperature. The tints are due to the formation of an oxide film on the surface and indicate to the workman the point at which the steel should be cooled off. Thus steel is tempered at 220° for razors and at 295° for watch-springs.

106. Metastable and Stable Equilibrium.—The Phase Rule in its standard or "reduced" form can only be applied to systems which have attained true equilibrium. If the number of phases found to be present in an alloy is not the same as the number that should exist according to the Phase Rule, we can conclude at once that the alloy has not attained true equilibrium and is actually existing in the metastable condition. Strangely enough, most of the well-known materials used in the arts are in a metastable state. Steel is a notable example of a material endowed with the capacity of persisting, so far as we know, indefinitely in the metastable condition. In fact, metal implements made thousands of years ago are found to be

still in the metastable condition today. This remarkable manifestation of hysteresis is due to solid-rigidity forces which prevent the internal adjustments demanded by the prevailing thermodynamic conditions.

In the case of alloy systems especially, the ideal state of stable equilibrium is seldom attained in practice, and there has been much discussion as to whether the equilibrium diagram should refer to the unattainable equilibrated state or to the metastable state. It is true that the alloy, as we find it, is in the metastable condition, but even so, it must be urged that the equilibrium diagram should refer to the state of stable equilibrium, since it is only under these conditions that the constitution of the alloy is definitely fixed. Ordinary alloys will aspire to this conditon when the rate of cooling is sufficiently slow, and the intermediate states of metastable equilibrium should therefore be referred to the true equilibrium diagram.

III. THE NATURE OF ALLOYS

Man's uniqueness as the sole tool-making animal of creation might yet have come to naught had not some unnamed genius, towards the end of the Stone Age, discovered the plastic metals, infinitely more responsive to man's deft craftsmanship. The final phase in the history of metals and man is concerned with the art of metallurgy, shortly to become a science.—L. R. VAN WERT

107. The Phase Diagram and the Properties of Alloys.—An alloy has been defined by a Committee of the Iron and Steel Institute as *a substance possessing the general physical properties of a metal, but consisting of two or more metals, or of metals with non-metallic bodies in intimate admixture, solution or combination with one another*. Two metals may give one or other of the equilibrium diagrams described in Chapter VII, and from these it is possible to obtain a general indication of the physical properties of alloys of various compositions. As examples of this kind we may refer briefly to the hardness and the electrical conductivity of alloys.

Hardness.—Pure metals are comparatively soft, but some of their alloys may be extremely hard. The basic connexion between the hardness and the type of alloy is illustrated in Fig. 114, which gives the equilibrium diagram and the corresponding hardness curve.

For the eutectic type of system the ideal hardness curve is practically a straight line extending from the hardness value of one metal to that of the other.   Intermetallic compounds

Composition   *Composition*   *Composition*
(a) Eutectic System (b) Intermetallic Compound (c) Solid Solution
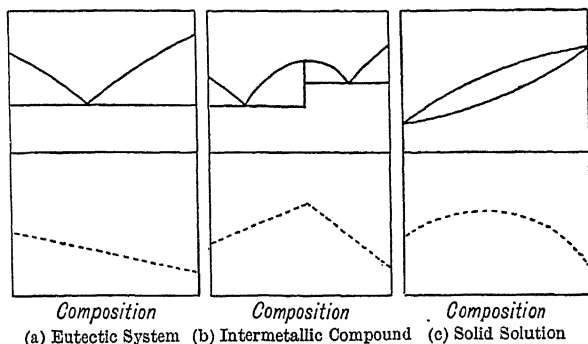
Fig. 114.   Ideal hardness curves of alloys of different types

are generally very hard and the hardness curve for such a system usually shows a maximum at the composition of the compound.   The compound Cu_3Sn, for example, is about twelve times as hard as copper.   Solid solutions are generally

Composition   *Composition*   *Composition*
(a) Eutectic System (b) Intermetallic Compound (c) Solid Solution
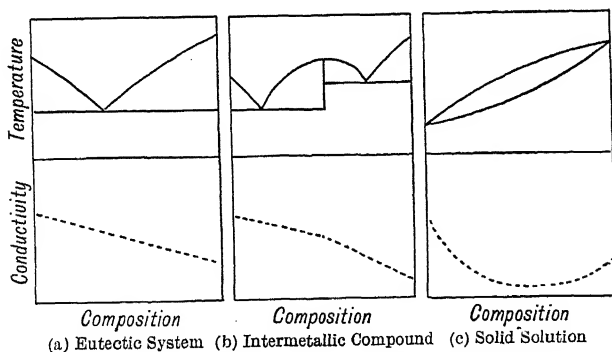
Fig. 115.   Conductivity curves of alloys of different types

harder than the constituent metals as indicated in the above diagram for completely miscible solid solutions.

Naturally, the experimentally obtained curves depart from the ideal curves, since the hardness depends, not only on the composition, but also on the grain size and other structural

features of the alloy. The alteration in the hardness of an alloy by heat treatment depends of course on the modification of these features.

Electrical Conductivity.—The conductivity of alloys is usually lower than that of pure metals. The connexion between conductivity and the type of phase diagram is shown in Fig. 115.

As might be anticipated, the conductivity of the eutectic alloy falls in a linear manner from the metal of high to the one of low conductivity. The conductivity of intermetallic compounds is generally lower than that of the more conducting component and sometimes considerably lower than either metal. The compound Mg_2Sn, for example, has an extremely low conductivity, although the separate metals are fairly good conductors. Solid solutions are likewise poor conductors, and it appears that the movement of the electrons or the "electron drift" is greatly hampered in a solid solution. Moreover, the change of conductivity with temperature or the temperature coefficient of resistance is much lower for solid solutions than for the pure metals. Solid solutions of nickel and chromium are widely used as resistance wire (" nichrome ").

Fig. 116. Interstitial solid solution with small atom " off-lattice "

108. **Primary Solid Solutions.**—The atoms in a pure metal are arranged in a three-dimensional lattice and when such a body incorporates another element in solid solution the atoms of the latter may be distributed in two different ways in the primary lattice :

(*a*) on the original lattice points of the first metal to produce a *substitutional solid solution* (cf. Fig. 90), e.g. *α*-brass in which zinc atoms take up positions occupied by copper atoms in the original lattice ;

(*b*) in the interstices of the original lattice to produce an *interstitial solid solution*, e.g. steel in which the carbon atoms lie in the interstices of the iron lattice, as depicted in Fig. 116.

The formation of the latter type of " off-lattice " solid solution is comparatively rare and occurs only when the solute atom is relatively much smaller than the atoms of the " host " metal. In the stainless steels both substitutional and interstitial solidution occur in one and the same alloy ; the nickel and chromium atoms take up their positions on the cubic lattice while the carbon atoms are located in the interstices of the lattice.

All these systems in which the basic or primary lattice of the solvent metal is preserved are termed *primary solid solutions*.

Order-Disorder Transformation. Superlattices.—Substitutional solid solutions may have the " guest " atoms disposed
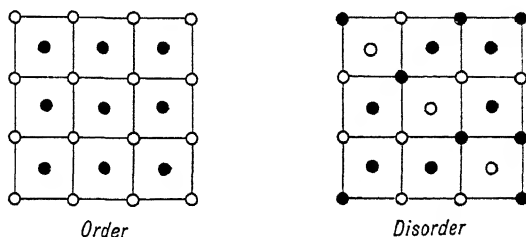
Order   Disorder

FIG. 117.   Ordered and disordered solid solutions

in an ordered or disordered array in the " host " lattice, as shown in Fig. 117.

At low temperatures the atoms of metal B arrange themselves in an ordered fashion so that they are regularly interspersed with those of metal A. But at high temperatures this order may disappear as a result of thermal agitation. In this way the ordered solid solution is transformed into a disordered solid solution.

To take an example, let us consider an alloy of iron and aluminium. At low temperature the solid solution has an ordered lattice, and the atoms are arranged in the following way along the diagonal of the cubic structure :

Order :   Al Fe Fe Fe Al Fe Fe Fe Al Fe Fe Fe,

but at higher temperatures some of the aluminium atoms leave their positions of " order " to replace iron atoms at other points and so produce a " disordered " structure :

Disorder :   Al Fe Fe Fe Fe Al Fe Al Fe Fe Fe.

The heat effect which accompanies the order-disorder transformation is very small and can only be measured by the differential couple method. The transformation is not a direct phase change, and since the alloy is strictly homogeneous throughout, the change finds no expression in the ordinary equilibrium diagram. But the X-ray spectograms reveal the existence of order since they have lines additional to those given by the disordered arrangement. These are called *superstructure lines* and the ordered solid solutions which give rise to them are said to have *superlattices*.

A disordered solid solution has a much lower electrical conductivity than the ordered solid solution. The ordering of a solid solution is effected by keeping the material in an annealing furnace at a suitable temperature for several days. The degree of ordering may be followed by determining the electrical resistance or by taking X-ray photographs of the material.[1]

109. **Secondary Solid Solutions.**—A *secondary solid solution* is one with a crystal structure different from that of either parent metal.

An alloy phase is simply a homogeneous, physically distinct and mechanically separable portion of an alloy system. In certain alloy systems we find a number of intermediate solid solution phases, each with a characteristic arrangement of atomic sites. These solid solutions are denoted by the symbols a, β, γ, δ, etc., according to their position in the equilibrium diagram. This is illustrated in the well-known brass diagram (Fig. 118).

Copper melts at 1083° and zinc at 419°; the upper curve is the liquidus and the lower curve the solidus. The latter shows a series of breaks corresponding to the peritectic transformation of the various solid solutions :

$$a \quad \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}} \quad \beta + \text{liquid},$$
$$\beta \quad \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}} \quad \gamma + \text{liquid},$$
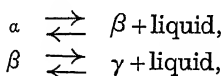
and so on. The other lines in the diagram show how the compositions of the various solid solutions change with temperature.

Pure copper has a face-centred cubic lattice and when zinc is added, the face-centred cubic lattice characteristic of copper

[1] Bragg, *J. Inst. Metals.*, 1935, **56**, 286 ; Williams, *Science Progress*, 1937, **32**, 15.

is retained although some of the lattice points are now occupied by zinc atoms. This is a primary solid solution and is termed the α phase. After adding about 32 per cent of zinc the α phase reaches saturation and a second phase makes its appearance. The structure of this phase is different from the original copper lattice and for this reason it is termed a secondary solid solution. Actually, it possesses a body-centred cubic structure, and since it is the second phase of the series it is designated
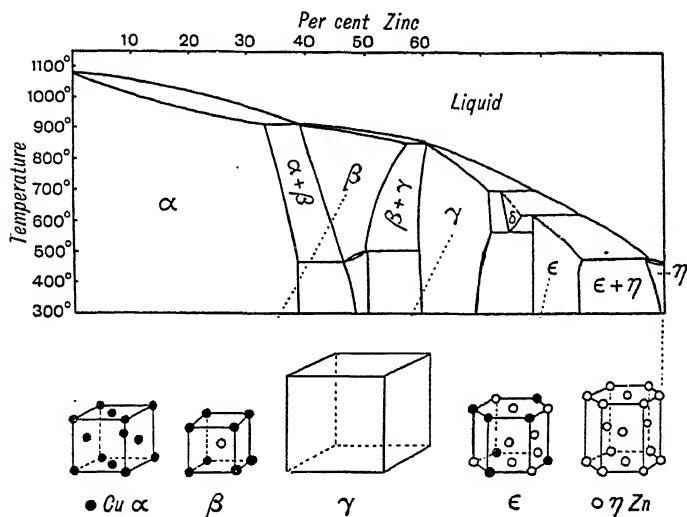
FIG. 118.   Alloy phases in the Copper and Zinc system

the β phase. A third secondary solid solution of copper and zinc is the γ phase which has a complicated cubic structure with 52 atoms in the unit cell. The fourth secondary solid solution is the δ phase while the next is the ϵ phase with a hexagonal close packed structure. Zinc itself has a hexagonal structure.

110. **The Hume-Rothery Rule.**—In 1926 Hume-Rothery observed that all β phases which had been examined by X-ray methods had a body-centred lattice, and boldly predicted that all other β phases would likewise have the same structure. With a view to explaining the occurrence of phases at analogous compositions he suggested that an alloy is a combination of electrons and atoms in a space lattice, and that the ratio of

the number of electrons to the number of atoms is the major factor determining the type of alloy structure.[1]

According to the Hume-Rothery rule there is a definite relation between the number of valency electrons and the number of atoms. Thus, β phases of composition $CuZn$, Cu_3Al and Cu_5Sn have the following electron : atom ratios :

Number of electrons : $Cu = 1$, $Zn = 2$, $Al = 3$ and $Sn = 4$;

$$CuZn = \frac{1+2}{2} = \frac{3}{2} ; \quad Cu_3Al = \frac{3+3}{4} = \frac{3}{2} ; \qquad \frac{5+4}{6} \quad \frac{3}{2}$$

For these phases the electron : atom ratio is $3/2$, and they all possess a body-centred cubic lattice. Although some exceptions are known the rule is found to be applicable to a large number of different alloys. The production of these structures has also been discussed from the standpoint of wave mechanics, the electrons being regarded as wave systems to be accommodated by the structure so that the potential energy is at a minimum.[2]

111. Intermetallic Compounds.—Metals are capable of combining together to form intermetallic compounds. They are prepared in normal fashion by melting the metals together in the required proportion and cooling the fused mass to ordinary temperature. Such compounds present several points of theoretical and practical interest among which we may mention the following :

(*a*) A metal never combines with a metal in its own sub-group of the Periodic Table. Copper, for example, does not form intermetallic compounds with silver or gold.

(*b*) The ordinary valency rules are not obeyed and formulae such as $PbMg$, $CuMg_2$, $AgMg_3$, Al_3Mg_4 and Au_2Mg_5 are quite common.

(*c*) Intermetallic compounds are usually hard and brittle.

(*d*) Intermetallic compounds are poor conductors of heat and electricity.

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[1] Hume-Rothery, *The Metallic State*, Oxford Univ. Press, 1931.

[2] Mott and Jones, *Properties of Metals and Alloys*, Oxford Univ. Press, 1936.

The remarkable rôle of the electron is further revealed in the electrical and magnetic properties of alloys. As a matter of fact, certain alloys containing as much as 88 per cent of iron are not in the least magnetic, while the *Heusler bronzes* composed of the feebly magnetic metals Mn, Cu and Al are nearly as magnetic as iron itself.

(e) X-ray analysis reveals that the various atoms are arranged in a characteristic, ordered space lattice.

(f) The chemical reactivity of an intermetallic compound may be greater or less than that of the constituent metals. The compound Mg_2Pb oxidises spontaneously at ordinary temperature, but there are other intermetallic compounds which are more inert than the parent metals.

Gases and liquids consist of discrete molecules but the term " molecule " has no corresponding implication in a solid alloy. We may, it is true, describe an alloy phase by a simple formula such as Mg_2Pb, but this does not imply that such a molecule exists as a definite entity in the alloy. The term " chemical combination " as applied to these metallic systems merely denotes a structure which is characteristically different from that of either of the pure components. An intermetallic compound is thus a phase of fixed composition in which the metals are present in fairly simple atomic ratios.

If a material is to be called an intermetallic compound because it has a definite composition with a simple atomic ratio, it should be borne in mind that such a combination is fundamentally different from the ordinary polar type of inorganic chemistry and the ordinary non-polar type of organic chemistry. In the circumstances it is best to define an intermetallic compound as *a phase of fixed composition in which the metals are present in fairly simple atomic ratios and in which some kind of electronic interaction has occurred between the metallic atoms.* From the X-ray examination of these materials Westgren concludes that an intermetallic compound is " something " between an ordered solid solution and a true chemical compound. The distribution of the atoms in the space lattice of an intermetallic compound is not determined solely by chance, and on these grounds it has been suggested that the bonding of the atoms occurs through a *metallic link* of a character intermediate between the polar link and the non-polar bond.

112. **The Constitution of Solids.**—In so far as the solid state is concerned, there is strong evidence for the belief that solid substances may be built up through the operation of physical and pseudo-chemical forces which simulate in some respects the true chemical forces responsible for the existence of ideal chemical compounds. In virtue of these forces we

may have the "intermediate states of union" found in solid solutions and possibly intermetallic compounds, as depicted in the scheme—

| Physical | Solid | Intermetallic | True Chemical |
| Mixture | Solution | Compound | Compound |

Approach to Ideal State of Chemical Combination
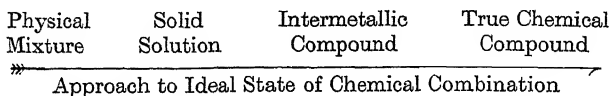
The relationships between these "states of union" are summarised in the following table :

TYPES OF SOLIDS

Type	Crystal Structure	Composition	P	C	Melting Point	Bonding
PHYSICAL MIXTURE	Two separate lattices	Variable	>1	>1	Melts over a range of temperature if not a eutectic mixture	No link of any kind between the components
SOLID SOLUTION	One fixed lattice which may be "ordered" or "disordered"	Variable	1	>1	Melts over a range of temperature if not a minimum or a maximum melting solid solution	Crystal forces
INTERMETALLIC COMPOUND	One fixed lattice, which is always "ordered"	Fixed	1	1	Fixed (at constant pressure)	Metallic link possibly involving a special kind of electron transfer or electron sharing, but ordinary valency rules not obeyed
TRUE CHEMICAL COMPOUND	One fixed lattice which is always "ordered"	Fixed	1	1	Fixed (at constant pressure)	Polar link involving electron transfer, or non-polar link involving electron sharing. Valency rules obeyed in each case

113. Amorphous Solids.—Amorphous substances, as the name implies, are materials devoid of crystalline form. They differ from pure crystalline bodies in the following particulars :

(a) They do not melt sharply but gradually soften over a wide range of temperature.

(b) When broken by a sharp blow they exhibit a conchoidal fracture. Unlike crystals, they do not suffer cleavage along

a particular plane and the fractured surface generally shows concave and convex rings.

(c) They flow in the manner of liquids under suitable conditions.

(d) They do not diffract X-rays or give rise to a diffraction pattern.

Amorphous solids are really supercooled liquids, and although they apparently exhibit the properties of solids it can be shown in many cases that they are capable of flowing like a liquid. Pitch, for example, when kept in a funnel for several months will flow out at the open end ; the slowness of the process is merely due to the extremely high viscosity of the material. Glass provides another familiar example of supercooled liquid, but in this case slow crystallisation may sometimes set in. This gradual crystallisation is found to occur in old glass apparatus and is termed *devitrification*.

Perhaps the most significant fact revealed by the X-ray examination of solid bodies is the extreme rarity of the truly amorphous state, for most so-called amorphous substances are found to betray some kind of organised structure under the searching scrutiny of the X-ray.

PRACTICAL METHODS

21. **To investigate a Two-component System and construct the Equilibrium Diagram.**—Various methods of thermal analysis are used according to the needs of the investigation and the nature and amount of material available. The chief methods are

    i. The Cooling Curve Method using a thermometer.

    ii. The Thaw-Melt Method.

    iii. The Cooling Curve Method using a Thermocouple.

    iv. The Heating Curve Method using a Differential Thermocouple.

    i. *The Cooling Curve Method.*—For ordinary laboratory experiments the apparatus (Fig. 119) consists of a wide test-tube provided with a thermometer and a stirrer. Let us suppose that the two components are naphthalene and

p-nitrotoluene. The freezing point of pure naphthalene is first determined by taking the cooling curve. For this purpose a known weight (6 g.) of naphthalene is placed in the tube and melted by immersing the tube in a heating bath at about 85°. When the contents are completely molten, the tube is removed from the heating bath, quickly wiped with a duster and placed in the cooling chamber as shown in Fig. 119. The liquid is stirred regularly and time-temperature readings are

taken as the liquid cools. This cooling curve gives the freezing point of pure naphthalene.

The same procedure is applied to mixtures containing 2 g., 4 g., and 6 g. of p-nitrotoluene, respectively. These cooling curves will show two arrests—the first corresponding to the liquidus and the second to the solidus.

The tube is cleaned out and the cooling curves of pure p-nitrotoluene and of mixtures containing known amounts of naphthalene (2 g., 4 g.) determined in the same way. The arrest points for the pure components and for the mixtures are plotted on graph paper, and the liquidus and solidus curves are drawn to form the complete equilibrium diagram.

The cooling curve method is quite suit-
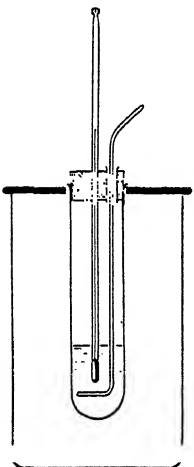
FIG. 119.   Determination of cooling curve.

able for investigating systems which do not form solid solutions.   Where solid solutions are formed the composition of the solid solution deposited from the liquid solution varies progressively with the temperature, and the cooling must be sufficiently slow to ensure complete equilibration by diffusion in the solid state. This requirement renders the method extremely tedious, and the thaw-melt method is invariably applied in these cases. The cooling curve method is also susceptible to errors arising from supercooling.   This difficulty may be overcome by making several experiments on the same sample and finding the arrest point at zero supercooling by extrapolation.[1]

ii. *The Thaw-Melt Method.*—This method depends upon the visual observation of the temperature at which the

[1] Andrews, *J. Phys. Chem.*, 1925, **29**, 914.

mixture begins to melt (thaw point) and the temperature at which liquefaction is complete (melting point).[1]

For the preparation of the mixture, quill tubing (12 cm. long and 7 mm. diameter) is sealed at one end to form a small test-tube. It is thoroughly cleaned and dried, and component A and component B accurately weighed into it so that the total weight of the mixture is about 0·2 g. The tube is then sealed in the blow-pipe flame, attached to a suitable holder and heated in a glycerine bath. When the mixture melts, the tube is thoroughly shaken in the bath to ensure complete mixing of the components. The tube is cooled quickly by immersion in a beaker of cold water, and the outside carefully dried. The tube is broken and the solidified mass removed to a watch-glass or small mortar where it is reduced to a fine powder.

The capillary tube in which the mixture is to be heated is made by drawing out an ordinary tube to form a capillary about 2 mm. in diameter as shown in Fig. 120. It is provided with a glass stirrer S made by drawing out a glass rod so that it works

FIG. 120.   The thaw-melt method

easily within the capillary. The powdered substance is introduced into the capillary and pressed down with the narrow rod S so that material occupies 3-5 mm. at the bottom of the tube.

For the actual observations, the apparatus illustrated in

[1] There is considerable ambiguity in the use of the term melting point. In our previous discussions, the point of incipient melting was termed the melting point. This is the same as the thaw point. The point at which liquefaction is complete (i.e. the point of incipient freezing) was designated the freezing point, but in the present connexion, it is called the melting point,—a designation approved by the Chemical Society.

Fig. 120 is very convenient.[1] It consists of a 600 c.c. beaker provided with an asbestos or wooden cover in which three holes are bored. The central hole is fitted with a cork carrying the thermometer. Above the adjacent hole a brass collar, cut on a slant, is bolted to the cover, so as to hold the capillary tube as shown in the diagram. By means of this arrangement, the substance can be held near the bulb of the thermometer, and the fused mass can be thoroughly stirred during the heating process. The glycerol or strong sulphuric acid used as bath liquid is stirred mechanically by a double-ring stirrer.

The bath is heated at a rate of 1° per 3-5 minutes, while the substance is illuminated by an electric lamp behind the beaker and is observed, if necessary, through a lens. By manipulating the stirrer and noticing particularly the outline of the substance against the sides of the capillary, it is not difficult to ascertain the point at which the mixture begins to melt (thaw point). The mixture is heated further while stirring continuously, and the temperature at which the fused mass becomes perfectly clear is taken as the melting point.

The thaw points and melting points of other mixtures, as well as of the pure components, are determined in the same way. The curve obtained by joining the thaw points is the solidus and that obtained by joining the melting points is the liquidus.

This method has the advantage of needing only minute quantities of the materials, and is undoubtedly the best method of investigating solid solutions.

The following substances are suitable for examination by either of the above methods :

Simple Eutectic Systems.—Naphthalene 80°-*p*-nitrotoluene 52° ; diphenyl 70°-phenyl carbonate 79° ; naphthalene 80°-phenanthrene 100° ; *a*-naphthol 94°-*β*-naphthylamine 112° ; naphthalene 80°-*p*-nitrophenol 114°.

Compound Formation.—Benzophenone 48°-diphenylamine 54° ; *s*-trinitrobenzene 122°-*β*-naphthylamine 112° ; antipyrene 113°-hydroquinone 169° (Two compounds formed).

Solid Solutions.—Naphthalene 80°-*β*-naphthol 122° (continuous series) ; *d*-carvoxime 72°-*l*-carvoxime 72° (maximum

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[1] This is a modification of the original method described by Rheinboldt (*J. prak. Chem.*, 1925, [ii] **111**, 242). It permits of actual stirring of the mixture during fusion and thus removes the danger of non-equilibration mentioned by Pounder and Masson (*J. Chem. Soc.*, 1934, 1357).

melting) ; naphthalene 80°-β-naphthylamine 112° (minimum melting).

22. **Thermal Analysis of an Alloy by the Thermocouple Method.**—The thermal analysis of an alloy system is usually made by means of a thermocouple which operates in virtue of the Seebeck or thermoelectric effect. If we have a closed circuit (Fig. 121 (a)) consisting of two different metals, welded together to form a junction, no current will be generated in the circuit if the temperature of the junction A is the same as that of the junction B. If now the junction A is kept at constant temperature by immersion in ice at 0°, while the

Cold Junction   Hot Junction
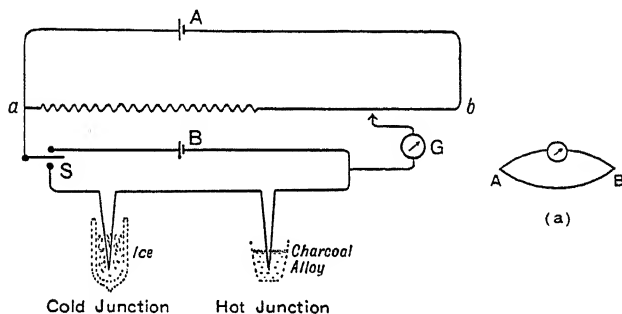
Fɪɢ. 121.   Thermal analysis by the thermocouple method

other junction is heated, an E.M.F. will be induced in the circuit and a current will flow from one junction to the other. A galvanometer included in the circuit will show a deflexion which will be a measure of the thermoelectric current. Since the strength of the current depends on the difference in temperature between the hot and cold junctions, the arrangement can be used to measure the temperature of a system. The best thermocouple consists of two wires, one of platinum and the other of an alloy of platinum and 10 per cent rhodium, welded into a junction. Base metal couples, such as the " alumel " type (Al and Mn), are much used at the present time. In order to protect the junction the thermocouple is always enclosed in a tube of porcelain or silica.

Although direct temperature recorders may be used for routine work it is customary to employ the potentiometer or " null " method for precision measurements. The principle of the method is illustrated in Fig. 121. A fall of potential

is maintained along the wire ab by means of the battery A so that the potential difference between any two points on the wire is proportional to the distance l between them. The potential difference is checked by means of the standard cadmium cell, which has a constant electromotive force E. This standard cell B is connected to the galvanometer G, and by means of the switch S and the contact C the potential difference along the wire is balanced against the standard potential difference between the terminals of the cell. The thermocouple is now brought into circuit (by reversing S) and the electromotive force E' between the hot and cold junctions is balanced against a length l' of the potentiometer wire. Then we have

$$\frac{E}{E'} = \frac{l}{l'} \quad \text{or} \quad E' = \frac{E.l'}{l}.$$

The thermocouple is calibrated by taking the freezing points or boiling points of standard substances, and a curve is drawn to show the relation between the measured electromotive force and the temperature difference of the two junctions.

The general arrangement of the apparatus used for taking cooling curves of alloy systems is indicated in the diagram. One junction is maintained at constant temperature by immersion in a Dewar or thermos flask charged with ice, while the other junction is immersed in a crucible containing the system under investigation. Suppose the two metals under study are lead and tin. The freezing point of pure lead is first determined in the following way. About 200 g. of the metal and a few grams of powdered charcoal are introduced into a fire-clay or graphite crucible and the metal melted in a small furnace. When the metal melts, the charcoal forms a layer on the surface and serves to prevent oxidation of the metal. The crucible is removed from the furnace and the thermocouple is arranged centrally in the molten metal. Time–electromotive force readings are then taken by means of a stop-watch or chronograph, while the metal is agitated by a rod of carbon or a suitable rocking device. After taking the cooling curve, the crucible is heated and time–electromotive force observations made as before in order to obtain a heating curve which may be used to check the previous cooling curve. The experiment is now repeated for mixtures of 160 g. Pb, 40 g. Sn ; 120 g. Pb, 80 g. Sn ; 100 g. Pb, 100 g. Sn ;

80 g. Pb, 120 g. Sn; 40 g. Pb, 160 g. Sn, as well as for pure tin.

The cooling curves are plotted on graph paper and the initial crystallisation and final solidification temperatures located on the curves. These data are employed to construct the liquidus and solidus curves of the complete equilibrium diagram as described previously.

23. **Thermal Analysis of Hydrates by the Differential Couple Method.**—This elegant method consists in balancing a couple inserted in a standard material against another couple placed in the substance under investigation. The
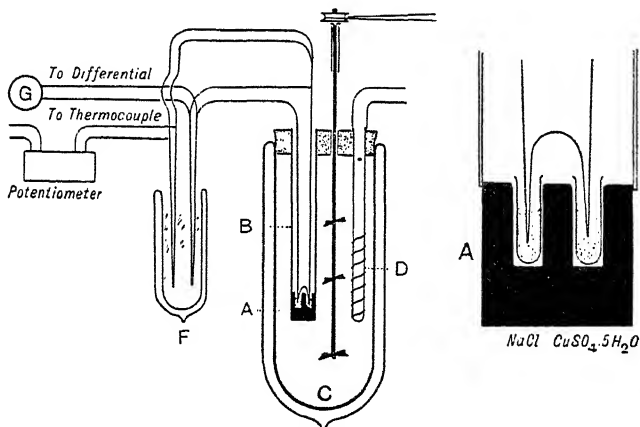
Fig. 122.   The differential couple method

standard material must give a regular heating (or cooling) curve and show no constitutional changes during the heating process. In this way it is possible to determine small differences of temperature (of the order of $0.01°$) between the standard material and the substance when both are heated in the same enclosure.

The principle of the method may be illustrated by the determination of the heating curve of copper sulphate penta-hydrate.[1] The heating cell A (Fig. 122) is a copper block with two holes into which slip two thin-walled glass tubes, one containing 1·5 g. of powdered $CuSO_4.5H_2O$ and the other an equal quantity of powdered sodium chloride. The latter

[1] Taylor and Klug, *J. Chem. Phys.*, 1936, **4**, 601.

is chosen as standard material to run against the copper sulphate because it suffers no phase transitions and has nearly the same specific heat as the hydrate. The cell is fitted into a glass tube B which is supported in a Dewar flask C provided with an electrical heater D and a stirrer. The cold junctions are immersed in a small Dewar flask F containing ice. The ordinary thermocouple (which measures the actual temperature of the heating chamber C) is connected to a potentiometer and galvanometer in the usual way, while the differential couple (which measures the difference in temperature between the copper sulphate and sodium chloride) is connected to a sensitive mirror galvanometer G. So long as the sodium chloride and the copper sulphate are heated at the same rate, the galvanometer does not indicate the passage of any current, but if there is a phase transformation or a change even in the character of the molecular motion, the resulting difference in temperature between the two systems will be recorded by the galvanometer.

In the actual experiment the temperature inside the chamber C is raised at a rate of 1° per minute. During this process the galvanometer shows deflexions corresponding to the slight thermal effects accompanying the change-over of the water molecules from the oscillatory to the rotational state as indicated in the diagram on p. 71. As the temperature is raised further, large thermal effects are recorded by both the differential and the ordinary thermocouples, each arrest corresponding to a definite phase reaction involving the break-down of the pentahydrate into tetrahydrate, trihydrate and monohydrate.

24. The Micro-examination of Steel.—The specimen of steel is cut by means of a hack-saw and rubbed along a smooth file or ground on the side of a smooth emery wheel or grindstone until flat. The file or wheel marks are removed by rubbing the specimen on coarse emery cloth placed upon a smooth sheet of glass. The small scratches produced by the abrasive are obliterated by rubbing on finer grades of emery paper, such as FF, O, OO and OOO. The fine scratches which remain after this treatment are removed by polishing the specimen on a revolving block covered with " Selvyt " cloth, which is moistened with water and impregnated with jeweller's rouge or finely powdered alumina. The perfectly polished surface should have a mirror-like appearance.

The next step is to remove the amorphous surface film or Beilby layer and expose the internal structure of the metal by etching. In the case of a steel the specimen is etched by immersion in a 2 per cent solution of nitric acid in alcohol or a saturated solution of picric acid in alcohol for about 30 seconds. After thorough washing under the tap in order to remove every trace of the etching reagent, the specimen is dried with alcohol.

When examined under the microscope pure iron is seen to consist of polygonal grains of ferrite as indicated in Fig. 123 (*a*). A low carbon steel (Fig. 123 (*b*)) shows dark areas of pearlite and white areas of ferrite ; under higher magnifications the

(*a*) Pure Iron showing polygonal grains of ferrite

(*b*) 0·6% Carbon Steel. Dark areas = pearlite. White areas = ferrite

(*c*) 1·2% Carbon Steel showing white iron carbide embedded in pearlite
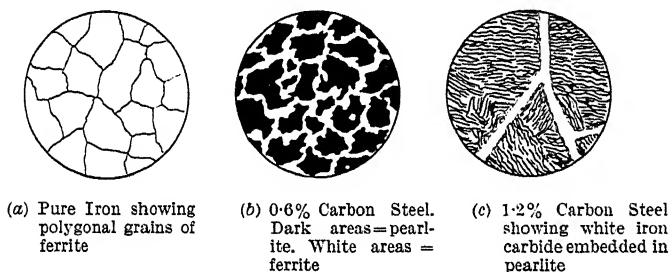
FIG. 123.   Typical micro-structures

dark areas are resolved into alternate lamellae of ferrite and iron carbide. In the high carbon steel (Fig. 123 (*c*)) iron carbide or cementite is seen embedded in pearlite. It appears as a brilliantly white area, while the pearlite is resolved into alternate lamellae of ferrite and iron carbide.

25. **Preparation of Solid Solutions.**—Potash alum and chrome alum are dissolved in water and the solution allowed to crystallise. Each crystal thus deposited is a solid solution or mixed crystal of the two substances. The concentration of the one solid in the other solid can be modified by altering the relative concentrations in the original liquid solution. Both potash alum and chrome alum crystals are octahedral and the mixed crystal is also octahedral.

26. **Preparation of Layer Crystals.**—One of the criteria of isomorphism is the ability of one substance to grow regularly and uniformly in a solution of the other substance to form a layer crystal.
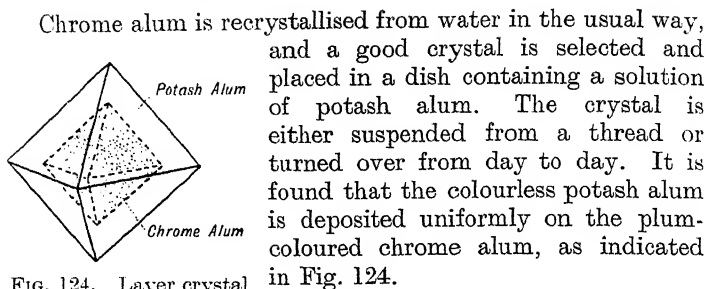
Chrome alum is recrystallised from water in the usual way, and a good crystal is selected and placed in a dish containing a solution of potash alum. The crystal is either suspended from a thread or turned over from day to day. It is found that the colourless potash alum is deposited uniformly on the plum-coloured chrome alum, as indicated in Fig. 124.

FIG. 124.   Layer crystal

A green crystal of nickel sulphate $NiSO_4.7H_2O$ may be coated with colourless zinc sulphate $ZnSO_4.7H_2O$ in the same way.

QUESTIONS

1. Summarise the types of diagrams which can be obtained from a study of the melting point and freezing point curves of two-component systems. Describe the procedure employed in investigating such systems in the laboratory.
(B.Sc., Hons., Birmingham.)

2. Describe the types of crystallisation phenomena which may occur when a liquid melt of two metallic components is allowed to cool (a) when no compounds are formed, (b) when compounds are formed. (M.A., St. Andrews.)

3. Describe what experimental measurements you would make and how you would use them to construct a phase diagram for a system of two metals. (B.Sc. Special, Reading.)

4. Illustrate with diagrams the equilibria in binary systems which give a continuous series of solid solutions. Describe the changes which occur during the solidification of such a system.
(Cambridge Tripos.)

5. Give some account of the process known as racemisation and indicate how it is possible to determine whether a solid substance is a true racemic compound or a mixture or conglomerate of d- and l- compounds. (B.Sc., Wales.)

6. Draw the Phase Rule diagram of the iron-carbon system and state the phase conditions represented by each area.
(B.Sc. Hons., St. Andrews.)

7. Indicate the principal features of the equilibrium diagram for iron and carbon. Show how the diagram can be used to interpret the influence of composition and of heat treatment on the properties of iron and steel. (Cambridge Tripos.)

8. What do you understand by the terms : *eutectic, eutectoid, peritectic, solid solution* ?   Illustrate your answer by means of diagrams.   (B.Sc. Metallurgy, Wales.)

9. Write short notes on (*a*) catalysis, (*b*) the " wiping " of a solder joint, (*c*) tin disease, (*d*) cementite, ferrite, pearlite.

(Inter. B.Sc., Edinburgh.)

10. What methods are used in the determination of the constitution and structure of alloys ?   Give an account of the results obtained in any two important cases.   (B.Sc., Reading.)

11. Give an account of the methods used to distinguish between solid solutions and chemical compounds in the metallic state.   (B.Sc., Bristol.)

12. Write an essay on " The Applications of the Phase Rule to the Study of Alloys ".   (B.Sc. Special, London.)

13. Discuss the relative merits of (*a*) thermal analysis and (*b*) electrical conductivity measurements in investigating the constitution of metallic alloys.   (B.Sc. Metallurgy, Birmingham.)

14. Write an essay on " Solid Solutions ".

(B.Sc., Birmingham.)

15. Give a short account of the modern views regarding the nature of " intermediate phases " of alloy systems.

(B.Sc., Birmingham.)

16. Discuss the formation of intermetallic compounds from the view-point of (*a*) the Law of Definite Proportions, (*b*) crystal structure, and (*c*) the Hume-Rothery ratio rules.

(Cambridge Tripos.)

CHAPTER IX

AQUEOUS SOLUTIONS

I will venture to predict that in five to ten years' time the subject will have advanced sufficiently to permit predictions of solubility with a fair degree of accuracy.—J. H. HILDE-BRAND (1936)

114. **The Saturated Solution.**—A saturated solution is defined as the *solution which is in equilibrium with the solid phase*. Students frequently fall into the error of describing a saturated solution as one " containing all the solute it can hold ", which is obviously incorrect since it is quite a simple matter to prepare a supersaturated solution containing more solute than the saturation value. When such a supersaturated solution is placed in contact with the solid phase it deposits the excess of dissolved substance and its concentration falls to the true saturation value.

· The behaviour in the presence of the solid phase provides an infallible test for the state of a solution. If the solution is *unsaturated* it will dissolve more of the solid ; if *saturated* it will remain unchanged ; if *supersaturated* it will deposit the excess solute until the strength of the solution has fallen to the saturation value.[1]

115. **The Solubility Curve.**—The solubility of most solids increases with temperature, but several cases are known in which the solubility decreases as the temperature of the solution is raised. The solubility curve is a *tc*-curve representing the change of concentration of the saturated solution with temperature and thus differs fundamentally from the vapour pressure or *pc*-curve of the solution (p. 67). The solubility curve may be straight or curved and may slope to

[1] Hildebrand mentions the case of a student who defined a supersaturated solution as one " containing more than it can hold " ! The definition is ludicrous merely for the want of the words " in the presence of the solid phase ".

the right or to the left. Moreover, it may exhibit flexures, maxima or minima, or suffer a sharp change of direction at a point. Some typical solubility curves are shown in Fig. 125.

Although the solubility curve may assume varied forms, its general direction can be predicted from Le Chatelier's principle (p. 14). It is evident, for example, that the solubility of the substance will increase with rise of temperature if the substance dissolves with the absorption of heat. The majority
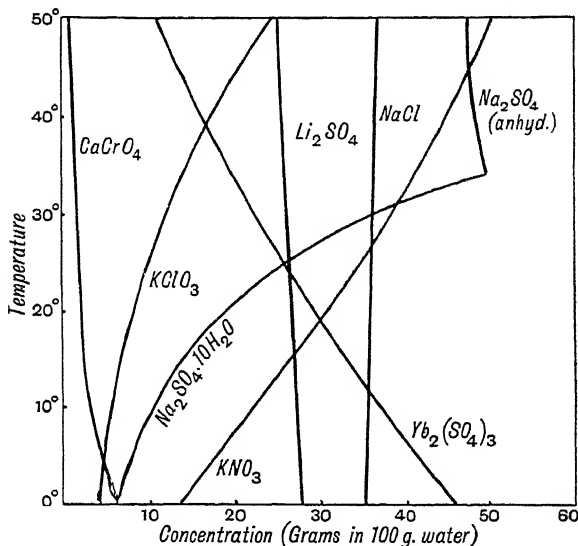
FIG. 125. Various forms of solubility curves

of substances behave in this way and give curves similar to those shown for potassium nitrate, potassium chlorate and sodium chloride. On the other hand, there will be a decrease in the solubility if the process of solution is accompanied by the evolution of heat. This behaviour is exhibited by comparatively few compounds, but is observed in the case of lithium sulphate, anhydrous sodium sulphate and certain calcium salts such as the acetate and the chromate. The phenomenon is especially prominent in the rare earth salts such as ytterbium sulphate and neodymium sulphate.

Discontinuous Curves.—The solubility curve of any given substance is continuous so long as the solid phase in contact

with the solution remains unchanged. A break or discontinuity in the curve always indicates that the solid phase is not the same, but has suffered a fundamental change in character. This change may involve (a) a physical change such as an allotropic transformation, or (b) a chemical reaction involving a change in the state of hydration.

In these cases we are really dealing with two distinct solubility curves intersecting at a point which corresponds to the transition of one state into another. The occurrence of a polymorphic change in the case of ammonium nitrate is revealed by the solubility curve (Fig. 126). Up to 32° the solubility curve is that of the β-form, but above this temperature the solubility refers to the γ-modification.
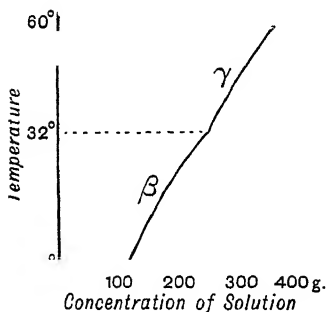
FIG. 126.   Solubility of allotropic forms

The other cause of a break in the solubility curve is a change in the degree of hydration of the salt, as may be seen in the solubility curve of sodium sulphate decahydrate (Fig. 125). At 32·4° the substance breaks down into anhydrous sodium sulphate, and the solubility curve above this temperature is that of the anhydrous salt.

" *Salting-out*."—Some organic substances which are soluble in water are only slightly soluble in solutions of certain salts, such as sodium chloride or sodium sulphate. Accordingly, if the salt is added to the aqueous solution of the organic material the latter will separate out from solution. This process is called "salting-out" and can be applied for separating alcohol, acetone and certain dyestuffs from their aqueous solutions. The principle is also utilised in large scale ether extraction of a solute from aqueous solution. At ordinary temperature 100 c.c. of water dissolve 8 c.c. of ether, but the solubility in a saturated sodium chloride solution is much lower. Accordingly, if the volume of solution to be extracted is large it pays to saturate the solution with common salt before adding ether.

116. **Classification of the Systems.**—Systems in which one

of the components is water present no fundamental differences from those discussed in Chapter VII, but in view of their importance to the chemist it is customary to consider them separately. According to the nature and properties of the solid phases these systems belong to one or other of three types :

Type I. Formation of Simple Eutectic or Cryohydrate.
Type II. Formation of Hydrate with Congruent Melting Point.
Type III. Formation of Hydrate with Meritectic or Incongruent Melting Point.

In most cases the equilibrium diagram refers to certain concentration limits which are specified on the concentration axis.

Type I. Formation of Simple Eutectic or Cryohydrate

117. Water and Potassium Chloride.—Potassium chloride does not combine with water to form a hydrate, and the
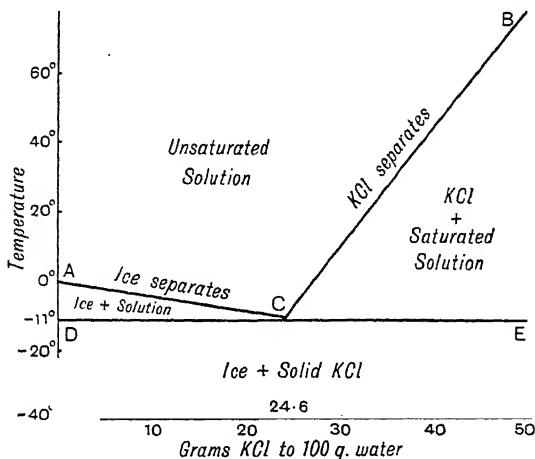
FIG. 127. Water and Potassium Chloride

equilibrium diagram for the binary system is shown in Fig. 127. The liquidus consists of two branches, AC representing the equilibrium between ice and the solution, and BC between

solid potassium chloride and the solution. The curve AC is called the freezing point curve and BC the solubility curve, although, actually, there is no fundamental difference between them.

If we cool a dilute solution of potassium chloride we find that pure ice separates when the temperature has fallen to a point on the curve AC. As a result of the separation of ice the solution becomes richer in potassium chloride and the equilibrium temperature follows the curve down to the point C. Similarly, if we cool a concentrated solution, pure potassium chloride is deposited when the temperature has fallen to a point on the curve BC, and as the solution becomes weaker in potassium chloride the system moves along the curve BC until the point C is reached. The point C is therefore a eutectic point at which ice and potassium chloride separate out together as a eutectic conglomerate. The horizontal eutectic line DE is the solidus below which all systems are entirely solid.

When, as in this case, one of the components is water the eutectic mixture is called a *cryohydrate*[1] and the corresponding eutectic point a *cryohydric point*. At the cryohydric point the solution freezes at constant temperature without change of composition.

Properties of Cryohydrates.—The fact that solid cryohydrates melt at constant temperature without change of composition led Guthrie to believe that they were definite chemical compounds, but such a supposition is untenable for the following reasons :

(a) the heterogeneous structure can be seen under the microscope ;

(b) the X-ray spectogram consists of two superposed but independent patterns ;

(c) the ratio of salt to water is seldom in simple molecular proportion and the agreement which is occasionally found is purely fortuitous ;

(d) the composition of the cryohydrate varies with the external pressure ;

(e) inert organic solvents, such as alcohol or acetone, may dissolve the ice and leave behind a network of the

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[1] The term, which was introduced by Guthrie of London, is derived from the Greek, meaning *frost water.*

(f) the heat of solution and the specific volume are the same for the cryohydrate as for a mechanical mixture of ice and salt in the same proportion ;

(g) unlike pure crystalline compounds the cryohydrates are usually opaque and ill-defined ;

(h) there are no definite indications of a chemical reaction during the formation of a cryohydrate.

A cryohydrate is thus nothing more than an intimate mechanical mixture of ice crystals and salt crystals, i.e. a eutectic mixture of the two components.[1] Actually, Rüdorph had given the correct explanation of cryohydrate formation several years before Guthrie's work.

The cryohydric point is the one and only point at which ice, the solid salt, solution and vapour are in equilibrium. It is in fact a quadruple point, and if we apply the ordinary Phase Rule we find that it represents an invariant system. Consequently, any change of pressure or temperature will cause one of the phases to disappear.

118. The Vapour Pressure Relationships.—The equilibrium between a simple salt and water may now be examined from the stand-point of vapour pressure, and for this purpose we make use of the pt-diagram shown in Fig. 128. If the solution is unsaturated we have two components (salt and water) in two phases (solution and vapour) and the system is bivariant. This implies that the vapour pressure is undefined and may have different values at the same temperature, since it is possible to change the concentration of the solution. On the other hand, if the solution is saturated and some of the solid salt is present as a third phase, the system is univariant. It follows therefore that a saturated solution has a fixed vapour pressure at each temperature.

In Fig. 128 the curve AO represents the vapour pressure or sublimation curve of ice, OC the vapour pressure curve of liquid water and OB the effect of pressure on the freezing point of water (cf. Fig. 5). Since the solute lowers the vapour pressure of the solvent the vapour pressure curve of the solution will lie below the curve OC. In fact, it will meet the curve AO at E, which is therefore the cryohydric point.

Let us assume that the solubility of the substance increases

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[1] Water and liquid HCN likewise form a eutectic system of this type (Coates and Hartshorne, *J. Chem. Soc.*, 1931, 675).

in normal fashion with rise of temperature. The vapour pressure of the solution is affected by two factors, the temperature and the concentration. Increase of temperature will cause a rise, but increase of concentration will cause a lowering of the vapour pressure. At low concentrations the temperature factor outweighs the concentration factor, so that the vapour pressure curve *EM* follows the general direction of the curve *OC*. At higher concentrations the concentration factor outweighs the temperature factor, and the vapour
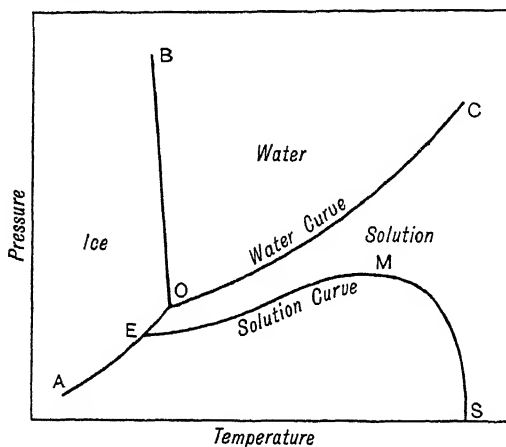
Fig. 128.   Pressure–temperature diagram for solution

pressure curve falls away from pure solvent curve to assume finally the value for the unadulterated salt. Owing to the interplay of these two factors the vapour pressure curve of the solution will be of the general form *EMS*.

Type II. Formation of Hydrate with Congruent Melting Point

This type of salt hydrate melts completely at one temperature and the liquid produced on fusion has the same composition as the original solid hydrate :

$$\text{S} \rightleftharpoons \text{liquid.}$$
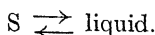
A hydrate which behaves in this way is said to have a congruent melting point.

119. (a) **Water and Ferric Chloride.**—Ferric chloride can form four hydrates of the following composition :

$Fe_2Cl_6 . 12H_2O$, $Fe_2Cl_6 . 7H_2O$, $Fe_2Cl_6 . 5H_2O$ and $Fe_2Cl_6 . 4H_2O$.
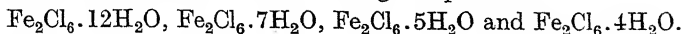
Each of these is stable and possesses a congruent melting point. Pioneer researches on this system were carried out by Bakuis Roozeboom, who determined the freezing point and solubility curves of the various hydrates as shown in Fig. 129.

The curve AB represents the lowering of the freezing
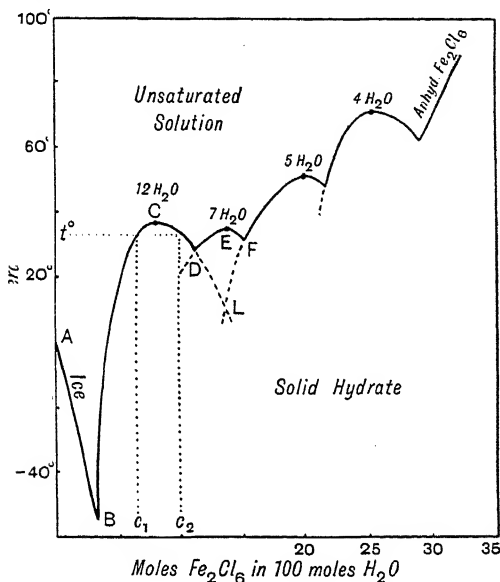
FIG. 129.   Water and Ferric Chloride

point of water by the addition of ferric chloride. The point B is a cryohydric point at which the solution is in equilibrium with ice and crystals of ferric chloride dodecahydrate $Fe_2Cl_6 . 12H_2O$. The curve BCD shows the equilibrium between solid $Fe_2Cl_6 . 12H_2O$ and the solution ; in other words, it is the solubility curve of the dodecahydrate. The point C (37°) is the melting point of the dodecahydrate, and here the liquid and the solid have the same composition. This point represents the highest temperature at which the hydrate can exist by itself or in contact with any solution of ferric chloride.

If we increase the amount of ferric chloride in the system

we find another hydrate $Fe_2Cl_6 . 7H_2O$ making its appearance at D, which is a eutectic point at which the four phases—dodecahydrate, heptahydrate, solution and vapour—exist in equilibrium. It differs from the cryohydric point only in so far as the two solid phases are hydrates, whereas in the cryohydric mixture one of the solid phases is ice.

It is of interest to note that the addition of either water or ferric chloride to a solution of composition represented by C will lower the freezing point and that the separating solid phase will be $Fe_2Cl_6 . 12H_2O$ in either case. Thus, at the temperature $t°$ there are two different solutions (of composition, c_1 and c_2) in equilibrium with one and the same solid phase, viz. the dodecahydrate. The two curves BC and CD give the solubility of $Fe_2Cl_6 . 12H_2O$ and it is evident therefore that this compound has two distinct solubilities in water. This phenomenon is called *retroflex solubility*. It is quite general and is always found in these systems which give rise to solid compounds with congruent melting points.

The curve DEF is the solubility curve of the heptahydrate which has a melting point at E (32·5°). At F the heptahydrate and the pentahydrate separate as a eutectic mixture. The pentahydrate and the tetrahydrate give similar equilibrium curves in which the maxima correspond to the melting points of the hydrates and the points of intersection to eutectic mixtures. Finally, beyond the tetrahydrate region we obtain the solubility curve of the anhydrous salt. If we apply the Phase Rule we find that all the melting points and all the eutectic points are invariant. The solidus lines have not been included in the diagram since they can easily be supplied by the student.

Prior to the researches of Roozeboom, only the hydrate $Fe_2Cl_6 . 12H_2O$ was definitely known, although the existence of the pentahydrate was also suspected. It was while exploring the solubility curve of the pentahydrate that Roozeboom noticed certain irregularities, which ultimately led him to the discovery of the heptahydrate. As may be seen from the diagram this hydrate is stable over a limited range only, and it is doubtful whether it would have been discovered without a phase-equilibrium study of this kind.

We see, therefore, that each hydrate registers its existence by a separate solubility curve. In this connexion, however, it is important to bear in mind that *the hydrate must be capable*

of existing in the solid state in contact with the solution. The Phase Rule is not concerned with the fate of the hydrate in solution. Whether the hydrate breaks down or ionises is of no moment, but it must be able to exist as a definite solid phase before it can signalise its presence by means of a separate saturation track in the equilibrium diagram.

120. (*b*) **Water and Calcium Chloride.**—The five hydrates of calcium chloride have the following formulae : $CaCl_2.6H_2O$,
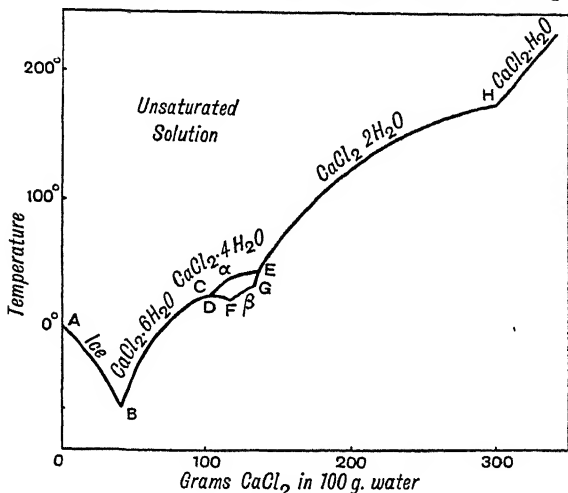
FIG. 130.   Water and Calcium Chloride

$CaCl_2.4H_2O$ (α), $CaCl_2.4H_2O$ (β), $CaCl_2.2H_2O$ and $CaCl_2.H_2O$. The equilibrium diagram (Fig. 130) is due to Roozeboom.

The lowering of the freezing point of water by calcium chloride is represented by the curve AB. At the cryohydric point B ($-55°$) the cryohydrate of ice and hexahydrate is in equilibrium with a liquid solution of the same composition. The curve BCD is the solubility curve of the hexahydrate and has a maximum at C. This is the congruent melting point ($30\cdot2°$) at which the hexahydrate fuses without change of composition and at constant temperature. The flattened form of the maximum indicates considerable dissociation of the hexahydrate in the liquid phase (p. 157).

Calcium chloride tetrahydrate can exist in two allotropic forms, each containing four molecules of water of crystallisation. The curve DE is the solubility curve of the α-tetra-

hydrate and FG that of the β-tetrahydrate. In this region certain invariant points are realisable on account of delayed or suspended transformation.

The curve EH is the solubility curve of the dihydrate and this meets the curve of the monohydrate at the eutectic point H. Only a portion of the monohydrate curve is shown in the diagram but it finally meets the solubility curve of the anhydrous salt $CaCl_2$ at about 260°. Calcium chloride must be heated well above this temperature if the material is to be used as a desiccant.

121. (c) **Water and Nitric Acid.**—The equilibria which obtain in this system are shown graphically in Fig. 131.
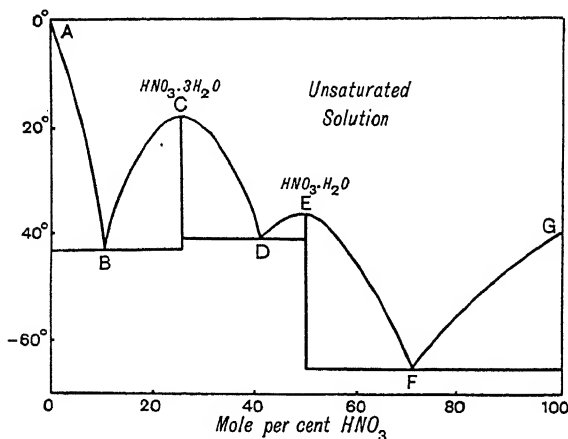
FIG. 131.   Hydrates of Nitric Acid

The solid phases which may be produced in the system are ice, nitric acid trihydrate $HNO_3.3H_2O$, nitric acid monohydrate $HNO_3.H_2O$ and anhydrous nitric acid HNO_3. The temperatures and compositions of the invariant points of the diagram are summarised below :

Point.	Temperature.	System.
A	0°	Pure water
B	$-43°$	Cryohydrate—ice$/HNO_3.3H_2O$
C	$-18·5°$	Trihydrate $HNO_3.3H_2O$
D	$-42°$	Eutectic—$HNO_3.3H_2O/HNO_3.H_2O$
E	$-38°$	Monohydrate $HNO_3.H_2O$
F	$-66·3°$	Eutectic—$HNO_3.H_2O/HNO_3$
G	$-41·2°$	Anhydrous or 100ᶜ

It is now believed that concentrated nitric acid is an equilibrium mixture of the true hydroxonium salt $[H_2OH]$ $[NO_3]$, the salt-like nitronium nitrate $[(HO)_3N]$ $[NO_3]_2$ and the pseudo-acid $HO.NO_2$, as indicated in the scheme :

$$\underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}} [H_2OH] [NO_3] \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}}$$
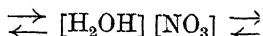
The amount of true hydroxonium salt in the almost anhydrous acid is negligibly small, but on the addition of water the nitronium nitrate is hydrolysed and this is followed by the conversion of the pseudo-acid into the hydroxonium salt or true acid. It is also found that the Raman line due to the NO_2 group fades out on the addition of water while a new line due to the NO_3 ion appears. It is evident therefore that the degree of ionisation and the constitution of nitric acid depend on the amount of water in the system.

122. (*d*) **Water and Sulphur Trioxide.**—Sulphur trioxide is able to exist in two allotropic modifications. The *a*-form is a
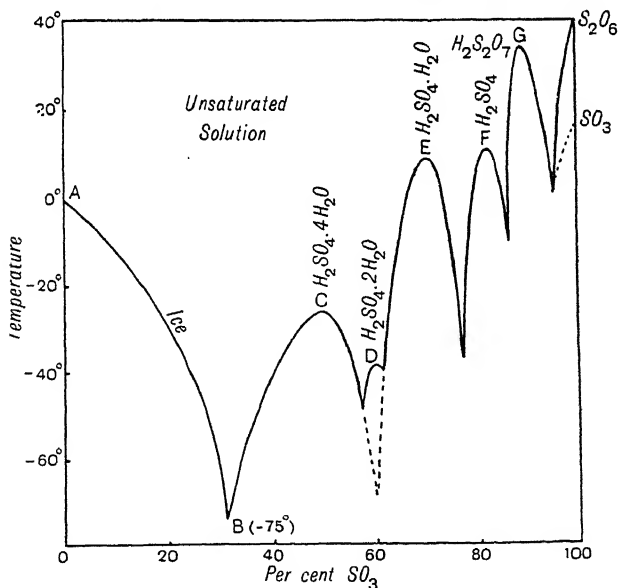
Fig. 132. Water and Sulphur Trioxide

liquid boiling at 46°, while the β-modification is a silky crystalline substance.

Sulphur trioxide is the anhydride of sulphuric acid and forms a series of compounds with water as indicated by the freezing point curves in Fig. 132. The maxima correspond to definite compounds: C ($-25°$)—sulphuric acid tetrahydrate $H_2SO_4.4H_2O$, D ($-39°$)—the dihydrate $H_2SO_4.2H_2O$, E ($8\cdot5°$)—the monohydrate $H_2SO_4.H_2O$ and F ($10\cdot4°$)—anhydrous sulphuric acid. Anhydrous sulphuric acid can dissolve further quantities of sulphur trioxide with the production of fuming sulphuric acid or oleum, and the point G corresponds to pyrosulphuric acid $H_2SO_4.SO_3$ or $H_2S_2O_7$, which melts at 36°.

The point B is the cryohydric point at which ice and sulphuric acid tetrahydrate separate as a cryohydric mixture, while the other points in the diagram correspond to normal eutectic mixtures. The dotted prolongations of the curves from C and E represent suspended transformation.

Type III. Formation of Hydrate with Meritectic or Incongruent Melting Point

The special characteristics of this type of hydrate are

(a) it undergoes partial fusion when heated to a certain temperature;

(b) it yields a new solid phase which may be a lower hydrate or anhydrous salt;

(c) it yields a liquid whose composition is different from that of the original hydrate:

$$S \rightleftarrows S' + \text{liquid.}$$
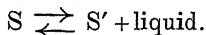
The temperature at which this change occurs is sometimes called an incongruent melting point or transition point. But the change is more deep-seated than an ordinary melting or an ordinary transition process. It is in fact a meritectic reaction involving the actual rupture of true chemical links (p. 159).

123. (a) **Water and Sodium Chloride.**—The equilibrium diagram (Fig. 133) may be regarded as a combined freezing point and solubility diagram. The freezing point curve AB gives the relation between the concentration of the solution and the temperature at which it is in equilibrium with ice. In other words, it shows how the freezing point is lowered

by the addition of salt. The solubility curve BC represents the equilibrium between the solution and the solid phase. This solubility curve refers, not to the anhydrous salt NaCl, but to the dihydrate $NaCl.2H_2O$, since it is the dihydrate which exists at temperatures below $0.15°$.

If we cool a solution of sodium chloride of concentration corresponding to the point a, ice separates out when the temperature has fallen to a point on the liquidus. This leaves the solution more concentrated and the system moves
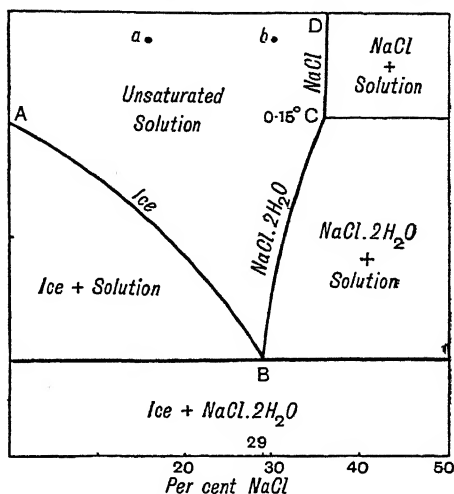
FIG. 133.   Water and Sodium Chloride

along the curve AB until at B the cryohydrate (ice/$NaCl.2H_2O$) is deposited at constant temperature ($-21°$). Similarly, a solution with the concentration of b becomes saturated when the temperature has fallen to a point on the curve CB and the dihydrate crystallises from the solution. The solution becomes weaker and the system traverses the curve CB, until at B, both ice and dihydrate separate out together at the constant cryohydric temperature.

At temperatures above the point C the dihydrate breaks down into the anhydrous salt as indicated by the equation

$$NaCl.2H_2O \overset{0.15°}{\underset{}{\rightleftarrows}} NaCl + Solution.$$
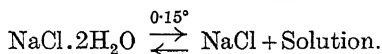
The point C is therefore the incongruent melting point or

transition point of the dihydrate, and it is obvious that the composition of the liquid produced is not the same as that of the original solid phase. The change is precisely similar to the meritectic reaction discussed on page 159. At all temperatures above 0·15° the stable solid phase is the anhydrous salt and the curve *CD* is therefore the solubility curve of anhydrous sodium chloride (cf. Fig. 125).

As may be seen from the diagram a solution of salt cannot exist in the stable state below the cryohydric temperature ; this temperature is therefore the lowest which can be produced by mixing together ice and salt. At the cryohydric temperature ice and salt (i.e. dihydrate) can exist in equilibrium with the corresponding cryohydric solution. Below this point ice and salt can exist side by side without affecting one another. Above the cryohydric temperature ice can only exist in contact with a solution of one particular concentration, and salt similarly with a solution of another concentration.

It is evident therefore that there can be no real equilibrium when we mix together ice, salt and water above the cryohydric temperature. If, for example, we mix the materials at −10° the water will tend to dissolve some of the salt, but this saturated solution will be too concentrated to be in equilibrium with ice. Ice will therefore melt, and the solution having become less concentrated will now dissolve more salt and this in turn will cause more ice to melt.[1] Clearly, heat must be supplied in order to melt the ice, and if it is not abstracted from an external source it must be derived from the system itself. In the latter case the temperature of the mixture will fall and if the mixture has the exact cryohydric composition the cryohydric temperature (−21°) will ultimately be reached. In an insulated system of this kind the temperature cannot fall below this value, since the solution can exist in equilibrium with both ice and salt at this point.

124. **Freezing Mixtures.**—A good freezing mixture should possess the following attributes :

(a) The cryohydric temperature should be low. This condition is satisfied if the salt is very soluble.

(b) The heat of solution should be high. This condition is satisfied if there is a rapid increase of the solubility with the temperature.

[1] These phase reactions underlie the process of thawing ice by sprinkling salt over it.

(c) The components should lend themselves to intimate admixture.

(d) The materials should be cheap.

Actually, the commonly-used freezing mixture of ice and salt is not a good one because the heat of solution of sodium

FREEZING MIXTURES

First Component	Parts by Weight	Second Component	Parts by Weight	Lowest Temperature
NH_4Cl	1	Ice	4	$-15.4°$
NH_4NO_3	100	Ice	131	$-17.5°$
$NaNO_3$	1	Ice	2	$-17.8°$
NaCl	33	Ice	100	$-21°$
Alcohol	77	Ice	73	$-30°$
H_2SO_4 (66%)	10	Ice	11	$-37°$
$CaCl_2.6H_2O$	10	Ice	7	$-55°$
Alcohol	..	Solid CO_2	..	$-72°$
Chloroform	..	Solid CO_2	..	$-77°$
Ether	..	Solid CO_2	..	$-77°$

chloride is very small and the heat absorbed is almost entirely due to the heat of fusion of ice. On the other hand, it has the advantage of cheapness and is readily prepared in the laboratory. A much better freezing mixture, conforming especially to conditions (a) and (b) above, may be made by mixing calcium chloride hexahydrate and ice. In fact, any system in unstable equilibrium which absorbs heat in passing to the more stable state can be used as a freezing mixture. Some examples of freezing mixtures are given in the above table.

Solid Carbon Dioxide.—Solid carbon dioxide is a white snow-like solid which is prepared by the rapid evaporation of liquid carbon dioxide (p. 239). It is finding many applications as a refrigerant and for preserving materials at a low temperature (p. 26).
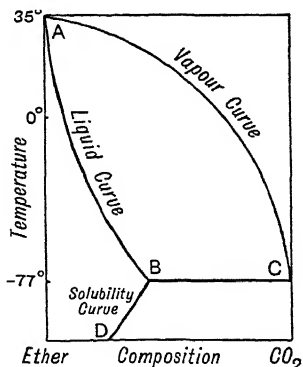
FIG. 134.   Ether and solid Carbon Dioxide

In the laboratory solid carbon dioxide and certain organic liquids of low freezing point make excellent freezing mixtures. The boiling point–composition diagram of the ether/solid CO_2 system is shown in Fig. 134. The point A represents the boiling point of ether and it is evident that the temperature of equilibrium is lowered by the addition of solid CO_2. The curve AB is the temperature–composition curve for the liquid and AC the corresponding curve for the vapour phase. The curve BD is the solubility curve, while the line BC gives the boiling point ($-77°$) of the three-phase system solid CO_2/ether/vapour.

When solid CO_2 is added to ether some of the CO_2 dissolves and some bubbles out, but when the temperature has fallen to $-77°$ the solid CO_2 remains as a mush in the ether.

125. (b) **Water and Sodium Sulphate.**—The equilibria between sodium sulphate and water are expressed graphically in Fig. 135.

The addition of sodium sulphate to water lowers the freezing point along the freezing point curve AB. The solubility of sodium sulphate decahydrate $Na_2SO_4.10H_2O$ increases with temperature as shown by the curve BC. Below $32.4°$ the decahydrate is quite stable in the presence of water and its solubility may be determined in the ordinary way (p. 96). Above $32.4°$ the decahydrate breaks down into the anhydrous salt Na_2SO_4 and solution, so that the solubility measured above this temperature refers to the anhydrous salt for this is the actual solid phase with which the solution is in contact. Unlike the decahydrate, the anhydrous salt is less soluble at higher temperatures and the solubility curve slopes backwards as indicated by CD.

The two solubility curves intersect at the point C ($32.4°$) and here the solution is saturated with respect to both solid phases. At this point therefore the four phases decahydrate, anhydrous salt, solution and vapour are in equilibrium and from the Phase Rule F = 0. The system will also be invariant if only three phases are present provided the pressure is kept constant. This is the case, for example, when the experiments are carried out under ordinary atmospheric pressure, for under these conditions the system decahydrate/anhydrous salt/solution will be invariant and exist at one temperature only. The temperature corresponding to C is the incongruent melting point of the decahydrate. The hydrate undergoes

transition or meritectic reaction with the formation of an-
hydrous salt and solution as expressed by the equation

$$Na_2SO_4 \cdot 10H_2O \overset{32 \cdot 4°}{\underset{\rightleftharpoons}{}} Na_2SO_4 + Solution.$$
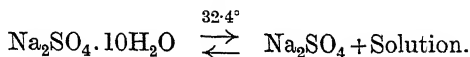
The dotted prolongation of the curve DC is realisable ex-
perimentally because the combination of the anhydrous salt
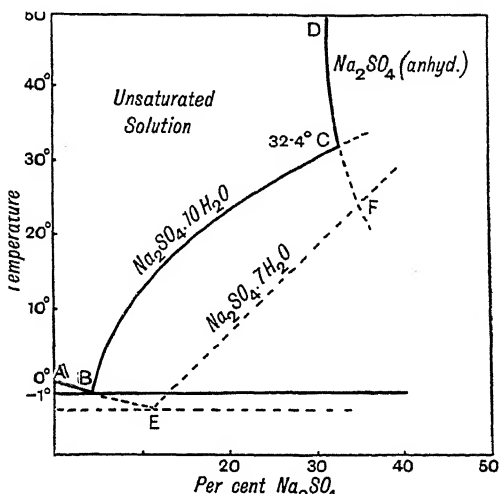
FIG. 135.   Water and Sodium Sulphate

with water just below $32 \cdot 4°$ is sufficiently slow to allow of the
measurement of the solubility before the salt changes into
the stable decahydrate.

If we prepare a warm saturated solution of the decahydrate
so that none of the solid remains and allow it to cool to the
ordinary temperature with adequate protection against the
access of particles of the decahydrate, we find that the solution
may be kept in this supersaturated state for a considerable
length of time. It frequently happens, however, that crystals
of a second hydrate $Na_2SO_4 \cdot 7H_2O$ separate from the solution.
This hydrate may also be prepared by adding alcohol to a
solution of sodium sulphate. Sodium sulphate heptahydrate
is more soluble than the decahydrate as may be seen from the
solubility curve EF. The point E is the cryohydric point at
which ice and heptahydrate separate. At the point F it is

possible for the three phases decahydrate, heptahydrate and solution to exist together, but the heptahydrate is unstable with respect to the decahydrate over the whole range of solubilities. The curves seem to indicate that there would be a transition of $Na_2SO_4.10H_2O$ into $Na_2SO_4.7H_2O$ at about $36°$ if the formation of anhydrous salt could be prevented. The transition point of the system

$$Na_2SO_4.7H_2O \quad \underset{\longleftarrow}{\overset{\longrightarrow}{}} \quad Na_2SO_4 + \text{Solution}$$
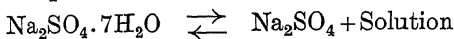
lies at about $24.4°$.

When anhydrous sodium sulphate is heated to $210°$ it suffers allotropic change into another crystalline modification.

126. (c) **Water and Sodium Carbonate.**—In the equilibrium diagram (Fig. 136), AB is the freezing point or ice curve, BC
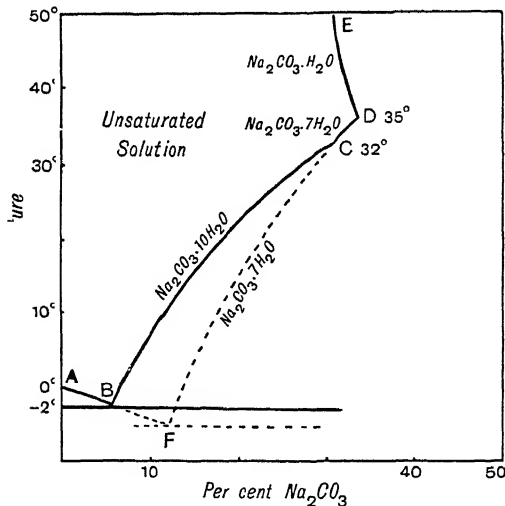
FIG. 136.   Water and Sodium Carbonate

the solubility curve of sodium carbonate decahydrate, CD that of the heptahydrate and DE that of the monohydrate. The point C is the meritectic or transition point of the system

$$Na_2CO_3.10H_2O \quad \overset{35.4°}{\underset{\longleftarrow}{\overset{\longrightarrow}{}}} \quad Na_2CO_3.7H_2O + \text{Solution},$$
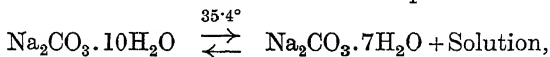
while D is the meritectic or transition point of the system

$$Na_2CO_3.7H_2O \quad \overset{32°}{\underset{\longleftarrow}{\overset{\longrightarrow}{}}} \quad Na_2CO_3.H_2O + \text{Solution}.$$
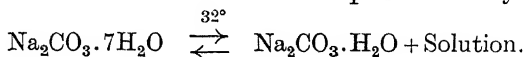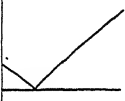
The heptahydrate has a short range of stability but can exist in the metastable condition along the curve CF. The heptahydrate may be prepared in the laboratory by adding alcohol to a saturated solution of sodium carbonate. Like the decahydrate (" washing-soda ") it effloresces in the air with the production of the monohydrate.

The monohydrate occurs naturally in the soda lakes of Egypt and is also found as an incrustation on the lava from Vesuvius. Above 35·4° the monohydrate is the stable solid phase in contact with water. The solubility curve DE shows that the monohydrate is less soluble as the temperature is raised. When a saturated solution of the hydrate is heated, crystals of the monohydrate are deposited but these dissolve again on cooling.

SUMMARY

BINARY SYSTEMS WITH WATER AS ONE COMPONENT

System	te-Curves	Characteristic	Example
Type I		Simple eutectic or cryohydrate. No hydrate formed	KCl which forms no hydrate
Type II		Formation of hydrate with congruent m.p. Hydrate melts completely : $S \rightleftharpoons$ liquid	Fe_2Cl_6 with 12, 7, 5, 4 H_2O $CaCl_2$ with 6, 4 (α), 4 (β), 2, 1 H_2O HNO_3 with 3 and 1 H_2O H_2SO_4 with 4, 2 and 1 H_2O
Type III		Formation of hydrate with meritectic or transition point. Partial fusion at incongruent m.p. $S \rightleftharpoons S' +$ liquid	$NaCl.2H_2O \rightarrow NaCl$ $\left.\begin{array}{l}Na_2SO_4.10H_2O\\Na_2SO_4.7H_2O\end{array}\right\} \rightarrow Na_2SO_4$ $\left.\begin{array}{l}Na_2CO_3.10H_2O\\Na_2CO_3.7H_2O\end{array}\right\} \rightarrow Na_2CO_3.H_2O$

PRACTICAL METHODS

27. **Preparation and Inoculation of Supersaturated Solutions.**—A supersaturated solution is prepared by completely

dissolving the solute at a higher temperature and then cooling the solution in the entire absence of the solid phase or of particles which may serve as nuclei of crystallisation. If such a supersaturated solution is " seeded " or inoculated with a small crystal of the solid, crystallisation sets in and the concentration of the solution falls to the true saturation value at that temperature.

Sodium thiosulphate $Na_2S_2O_3.5H_2O$ melts or dissolves in its water of crystallisation when heated above 48·5°. Actually, this involves a meritectic dissociation of the hydrated crystals according to the equation

$$Na_2S_2O_3.5H_2O \qquad Na_2S_2O_3$$
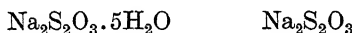
but at higher temperatures the anhydrous salt dissolves completely in the liberated water to form a clear solution. The phenomenon may be observed by fusing a quantity of the hydrated crystals in a test-tube and then raising the temperature to about 65° so that the substance forms a clear solution. The test-tube is now plugged with cotton-wool (to prevent the intrusion of " crystal germs " or dust particles) and allowed to cool to the ordinary temperature. The thick transparent supersaturated solution shows no signs of crystallising, but when a minute crystal of sodium thiosulphate is dropped into the solution, crystallisation occurs with considerable evolution of heat. Similar experiments may be made with a supersaturated solution of sodium sulphate, which may be prepared by heating 5 grams of the decahydrate and about 2 c.c. of water to about 55°. Usually, the inoculating crystal must be either the same substance or an isomorphous solid.

A supersaturated solution will crystallise without recourse to inoculation provided the conditions are suitable for the formation of nuclei and for their growth (p. 52). In so far as ordinary crystallisations are concerned, it is clear that if the conditions are such that the rate of formation of nuclei is small and the rate of growth is large, then a few large crystals will be formed. If, on the other hand, the rate of formation of nuclei is large and the rate of growth is small, we shall obtain a large number of small crystals. The latter conditions are always desirable when purifying a solid by crystallisation, since small crystals occlude impurities to a lesser extent than large ones.

28. **Preparation of a Solid CO_2-Ether Freezing Mixture.**—
A cloth bag is tied to the nozzle of a carbon dioxide cylinder
and the cylinder brought to the inverted position as shown in
Fig. 137.   The valve is quickly opened so that the liquid
carbon dioxide escapes and cools itself by rapid evaporation.
As a result of this process the carbon dioxide is frozen to a
white snow-like solid.   After closing the cylinder, the carbon
dioxide snow is transferred on a wooden
spoon into a Dewar flask containing
ether or alcohol.   Sufficient " snow " is
added to bring the temperature of the
liquid to the desired value.   The tem-
perature may be maintained at this
value by the further addition of small
quantities of the " snow " from time to
time.   The minimum temperature which
may be reached in this way is $-77°$.
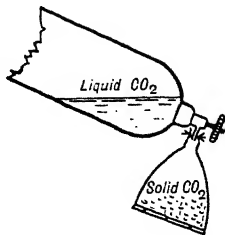
FIG. 137.   Preparation
of solid CO_2

Solid carbon dioxide, known com-
mercially as " dry ice," may be stored
for long periods in a Dewar vessel. The material may be
handled lightly without danger since the rapid evolution of
gas from the surface prevents actual contact of the cold solid
with the skin.   If, however, the substance is pressed against
the skin a serious " burn " may result owing to the freezing
of the water in the flesh tissues.

QUESTIONS

1. What do you understand by a supersaturated solution ?
Describe in detail how you would prepare such a solution, mention-
ing the salt you would employ.   How might the degree of super-
saturation be determined in a particular case ?

(Cambridge Higher School Certificate.)

2. What is meant by the terms *saturated* and *supersaturated* as
applied to solutions ?   Give an outline of any method of deter-
mining (and expressing) the solubility of a salt in water.

The temperature-solubility relations of many salts are repre-
sented by discontinuous curves.   Sketch the simpler *types* of
curve that are encountered and explain briefly their significance.

(Higher Certificate, Central Welsh Board.)

3. State the Phase Rule, defining all the terms used. Make use of the Phase Rule to explain the occurrence of cryohydrates.
(B.Sc., London.)

4. Sulphuric acid is said to form solid hydrates of definite composition. How would you proceed to test this statement and to ascertain the composition of the hydrates.
(London Higher School Certificate.)

5. Discuss from the point of view of the Phase Rule the systems formed from water and a salt which gives more than one hydrate.
(B.Sc., London.)

6. Solutions of common salt in water may be in equilibrium with crystals of salt or ice or both. Draw the form of the curves representing the relation between the temperature and the concentration of the solution in equilibrium with (a) ice and (b) salt.

Explain every part of the diagram. Comment on the term cryohydrate. Explain why ice and salt provide a good freezing mixture.
(Higher Certificate, Central Welsh Board.)

7. Write a concise account of the system sodium chloride and water in terms of the Phase Rule.
(B.Sc., Punjab.)

8. Under what conditions is it possible to obtain from an aqueous solution of sodium sulphate (a) ice, (b) hydrated sodium sulphate, (c) anhydrous sodium sulphate ? Give an explanation of the procedure necessary in each case.
(Oxford and Cambridge Higher Certificate.)

9. Anhydrous sodium sulphate is added to water at 100° and the system, continuously stirred, is allowed to cool to the ordinary temperature. Describe what takes place during the cooling process.

Indicate as nearly as possible the conditions under which the following systems may exist :

(a) Glauber's salt, solution, vapour ;
(b) Glauber's salt, anhydrous sodium sulphate, vapour ;
(c) ice, solution, vapour.
(B.Sc., Leeds.)

10. Discuss the implications of (a) the critical temperature of a pure substance, (b) the critical solution temperature of a liquid pair, (c) the maxima and minima shown by certain solubility curves.
(B.Sc., Leeds.)

11. The figures given below are the freezing points of aqueous solutions of hydrogen iodide at various concentrations, expressed as grams hydrogen iodide per 100 grams of water.

Concentration	Freezing Point	Concentration	Freezing Point
41·5	− 20·0°	190·0	− 40°
72·5	− 50·0	203	− 49
86·0	− 70·0	220	− 48·5
111·0	− 60·0	236	− 48·0
144·0	− 40·0	260	− 51·0
160·0	− 36·5	277	− 56·0
177·0	− 35·5		

Construct a diagram from these figures and state what conclusions can be drawn from it (I = 126·9).   (B.Sc., Wales.)

12. Discuss the vapour pressure curves and solubility curves of salt hydrates from the point of view of the Phase Rule. In particular explain how it is possible to detect the existence and composition of hydrates which are unstable.

(B.Sc., St. Andrews.)

13. In the light of Phase Rule principles give explanations of the following :

(a) that no amount of a chemical drying agent will remove *all* the water vapour from a quantity of gas ;
(b) the use of the transition temperature of Glauber's salt as a fixed point in thermometry ;
(c) the failure to obtain a deposition of solid hydroxide by the evaporation of a solution of sodium hydroxide at atmospheric pressure ;
(d) the " salting-out " of many organic liquids from aqueous solution by the addition of common salt.

(B.Sc., Manchester.)

CHAPTER X

THREE-COMPONENT SYSTEMS

Nature, always working by law, is always consistent, always inexorable.—SIMMONS

127. Variance of Ternary Systems.—The principles underlying the interpretation of the equilibria in three-component systems are essentially similar to those described in the case of binary systems.

According to the Phase Rule the number of degrees of freedom in a three-component system is given by

When the three components exist in one phase we have $P = 1$ and $F = 4$. Hence, the system will not be completely defined unless the four internal variables temperature, total pressure and the concentration of two of the components have been fixed.

A three-component system will be invariant $(F = 0)$ when five phases co-exist in equilibrium, and the point at which all five are stable together is called a *quintuple point*.

128. Representation of Ternary Systems.—The variations in concentration of three-component mixtures are conveniently expressed by means of triangular diagrams.

The most popular method was introduced by Sir George Stokes and used extensively by Roozeboom. The composition of the ternary mixture is represented by a point within an equilateral triangle, whose side is made equal to 100 per cent and is suitably divided into a number of equal parts. In Fig. 138 (a) the apex A represents the pure component A, i.e 100 per cent of A. Mixtures containing 80 per cent A will be represented by points on the 80 line drawn parallel to the opposite side, while mixtures containing 60 per cent will be represented on the 60 line, and so on. Similar methods are

adopted in order to represent the percentages of B (Fig. 138 (b)) and of C (Fig. 138 (c)).

If now we combine the three diagrams we obtain Fig. 139, which gives a complete representation of the composition of the ternary mixture. Each corner of the triangle represents a
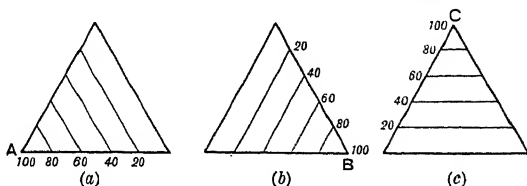
138. Construction of triangular diagram

single component or pure substance. A point on the side of the triangle corresponds to a binary system. Thus the point P represents a two-component system containing 40 per cent A and 60 per cent B. A point within the triangle corresponds to a ternary mixture. In any equilateral triangle the sum of the distances of a point inside the triangle (as measured by lines drawn parallel to the sides) is a constant and is always equal to the length of the side of the triangle. Thus the point M represents 40% A + 40% B + 20% C.

Other methods have also been used for representing ternary systems. Thus, Gibbs employed an equilateral triangle and made the height equal to 100 per cent, while Philip utilised a right angled isosceles triangle for the same purpose. All these methods are alike in so far as the apex represents a unary, a point on the side a binary, and a point inside the triangle a ternary system.
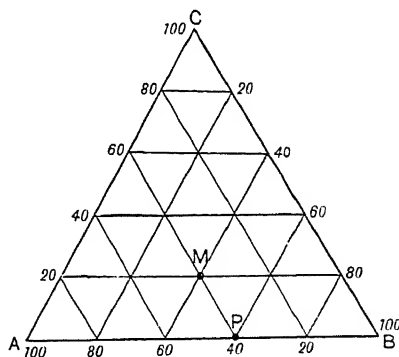
FIG. 139.   Triangular diagram for three components

129. **Typical Three-Component Systems.**—If the three components are gases they will mix completely to form a homogeneous system. Such systems have little interest in connexion with the Phase Rule.

When the three components are liquids, different types of systems are possible according as the liquids are completely immiscible, completely miscible or partially miscible. The chief interest, however, centres around those liquids which are partially miscible, and such systems may belong to one of the following types :

Type I. Formation of One Pair of Partially Miscible Liquids.

Type II. Formation of Two Pairs of Partially Miscible Liquids.

Type III. Formation of Three Pairs of Partially Miscible Liquids.

Partially Miscible Liquids

130. **Type I. Formation of One Pair of Partially Miscible Liquids.**—A good example of this type is furnished by the ternary system chloroform, water and acetic acid at ordinary temperature.

Chloroform and water are only slightly soluble in each other, but each can dissolve in all proportions in acetic acid.

Two liquid   One liquid
phases   phase

Fig. 140. Miscibility of Chloroform, Water and Acetic Acid

When, therefore, we gradually add acetic acid to the heterogeneous mixture of chloroform and water the mutual solubility of the latter substances will be increased, and if sufficient acetic acid is added, a point will be reached when a single homogeneous liquid phase is produced, as indicated in Fig. 140.

Actually, the acetic acid distributes itself between the two liquids so that two conjugate ternary solutions are in equilibrium. With the addition of further acetic acid, the compositions of the successive conjugate solutions become more nearly the same until, finally, a point is reached at which the two solutions are identical. At this miscibility point the mixture forms one homogeneous phase.

The Isothermal Equilibrium Diagram.—Adopting the conventional triangular diagram the equilibria at 18° may be represented as shown in Fig. 141. When chloroform and water

are thoroughly shaken together, some of the water dissolves in the chloroform and some of the chloroform in the water, so that we obtain two liquid layers or solutions, whose compositions are represented by the points a and b, respectively. If now we add a small amount of acetic acid it will distribute itself between the two layers, and the compositions of the two ternary conjugate solutions will be given by the points a_1 and b_1, respectively. The straight line a_1b_1 joining the two points is called a *tie-line*.

When more acetic acid is added we obtain a new pair of ternary solutions, whose compositions will be represented by
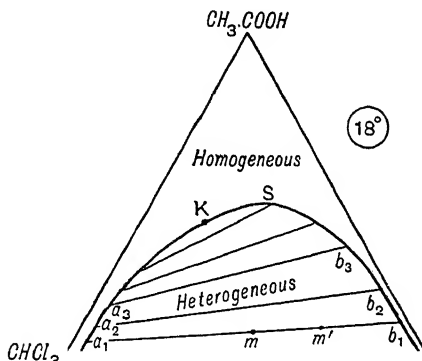
FIG. 141.   Isothermal equilibrium diagram for
Chloroform, Water and Acetic Acid

the points a_2 and b_2, and so on. With the continued addition of acetic acid the compositions of the two phases become more and more similar, while the tie-lines become shorter and shorter, until they finally shrink to a point at K. This point is called the *critical* or *plait point*. The curve aKb drawn through the series of miscibility points is called a *binodal* curve to indicate that there are two related values of the miscibility. The tie-lines are not parallel, but slope upwards on the water side, because the aqueous layer dissolves more acetic acid per unit volume than the chloroform layer. For the same reason the critical point K at which the tie-lines shrink to a point is not at the summit of the curve.

The curve aKb represents the boundary between heterogeneous and homogeneous systems. A point in the region outside the curve represents a homogeneous liquid phase

while a point inside the curve corresponds to a heterogeneous mixture of two liquid phases. If, for example, the three components are put together so that the composition of the mixture is represented by the point m the system will separate into two layers having the compositions a_1 and b_1, respectively. Every mixture whose composition is given by a point on the same tie-line will separate into the same liquid phases, but the relative amounts of the two phases will depend upon the position of the point on the line. Thus, the compositions of the two phases in mixtures at m and m' will be the same, but the relative volumes of the layers will be different.

According to the Phase Rule

$$F = 5 - P,$$

but if we keep the temperature and the pressure constant we have

If, therefore, the system exists as one liquid phase it will have two degrees of freedom and will be represented by some point
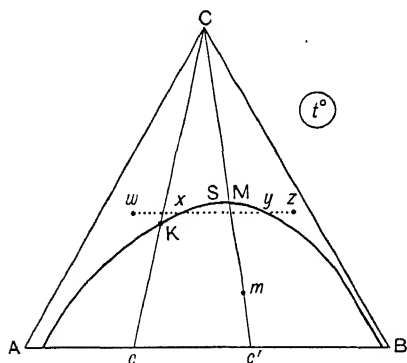
FIG. 142. The true critical point and retrograde solubility

in the region outside the curve aKb. Along the binodal curve there will be two phases, so that a system represented by a point on this curve will be univariant.

The True Critical Point.—The binodal curve comprises a series of miscibility or limiting points for systems of different compositions, and it should be noted that the true critical point is only realised when the original chloroform/ water mixture is of a certain composition. If, for instance, we add acetic acid to a chloroform/water mixture in the proportion represented by c' (Fig. 142) the resulting ternary mixture, say of composition m, will separate into two conjugate layers as

described above. In fact, having started with chloroform and water in the ratio corresponding to c', all ternary mixtures of the series will be represented by points on the straight line $c'mC$. At M, the miscibility point, the mixture becomes homogeneous, but this does not correspond to the shrinking of the tie-lines to a point. This occurs only at the critical point K, and to realise this point we must start with a mixture of chloroform and water in the proportions represented by c.

In applying the Phase Rule to the system at the critical point we have to take into account the additional restriction that the two phases have identical compositions at this point. If temperature and pressure are kept constant, we have

$$F = 3 - P—\text{Identity Restriction,}$$
so that $\qquad\qquad F = 0.$

If the experiments are carried out under constant atmospheric pressure the position of the binodal curve will depend only on the temperature, and the critical point will be perfectly defined for each temperature. In the case of a binary system (p. 100) the critical solution temperature is perfectly defined if the pressure is constant, but both temperature and pressure must be kept constant if the ternary critical point is to have a fixed value. The critical solution point of a binary system is indicated in degrees centigrade, but the critical point of a ternary mixture is expressed in terms of concentration with reference to one particular temperature.

Retrograde Solubility.—Since the critical point does not lie at the summit of the binodal curve, it is possible to change the state of the system above the critical point by simply altering the relative amounts of chloroform and water. If we alter the chloroform/water ratio in the ternary system at w (containing more acetic acid than at K but less than at S), the system will traverse the line wz. In this process the system will become heterogeneous at x and again homogeneous at y. This alternation of homogeneity and heterogeneity is called *retrograde solubility*, and is always observed when the critical point lies below the summit of the boundary curve.

Systems of this type are produced by many other ternary mixtures such as water, ether and alcohol, and lead, zinc and silver.

131. **The Effect of Temperature.**—If the experiments are

carried out under constant pressure the position of the binodal curve and of the critical point will depend only on the temperature. The change of composition with temperature may be represented by means of a right prism with the temperature measured vertically as shown in Fig. 143 (a). In this way the binodal curves obtained at different temperatures form a binodal or boundary surface. Two cases call for special mention.

(1) *No Real Critical Temperature.*—A ternary system which does not show a real ternary critical temperature is illustrated in Fig. 143. The curve *akb* is the binodal or iso-

(a) Space model   (b) Projection on base
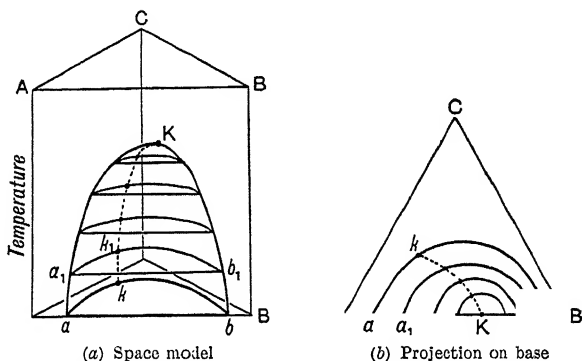
Fig. 143. No real ternary critical solution temperature

thermal curve for the three components A, B and C at a certain temperature. The curve $a_1k_1b_1$ is the binodal curve for the same system at a higher temperature. The series of binodal curves corresponding to different temperatures sweep out the tent-shaped binodal surface with the summit K in the plane $ABBA$. As the temperature is raised, the amount of component C in the critical mixture becomes less and less, until, finally, at K, only the two components A and B are present. The curve aKb is therefore the miscibility curve of the binary system A/B with the critical solution temperature at K.

Such a ternary system does not possess a real critical solution temperature, and this is brought into prominence by projecting the isothermals on to the base of the prism as shown in Fig. 143 (b). Since the component C is absent from the uppermost critical mixture, the point K is simply the critical

solution temperature of the system A/B and therefore lies on the side AB of the base of the prism.

(2) *Real Critical Solution Temperature.*—A system showing a real ternary critical solution temperature is represented in Fig. 144 (*a*). The curve $ak'b$ is the miscibility curve for the binary system A/B and lies in the plane $ABBA$. The binodal curves for the ternary systems are akb, $a_1k_1b_1$, etc., and the whole series sweeps out a helmet-shaped binodal surface with the summit K inside the body of the prism. In this case the point K is a real ternary critical solution
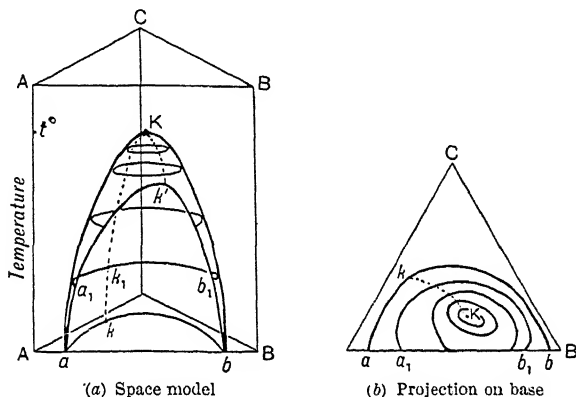
(*a*) Space model   (*b*) Projection on base
Fig. 144.   Real ternary critical solution temperature

temperature. Above $t°$, the temperature of this critical point, the three components are miscible in all proportions and form one homogeneous liquid phase. If we project the isothermals on to the base of the prism as in Fig. 144 (*b*) we find that the critical point K lies inside the triangle.

Water, acetone and phenol give rise to a system of this type with a critical solution temperature at 92°.

132. **Type II. Formation of Two Pairs of Partially Miscible Liquids.**—An example of this type is furnished by the three components water, alcohol and succinic nitrile $C_2H_4(CN)_2$.

Water and alcohol mix together in all proportions ; water and succinic nitrile form two liquid layers between 18·5° and 55·5° ; alcohol and succinic nitrile form two liquid layers between 13° and 31°. Accordingly, if the experiments are carried out between these temperature limits, we obtain two binodal curves ak_1b and ck_2d as shown in Fig. 145. A point

inside the areas ak_1b and ck_2d represents a heterogeneous mixture of two ternary solutions, while a point outside the curves corresponds to a homogeneous ternary solution.
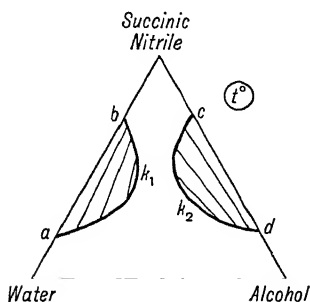
FIG. 145.   Two pairs of partially miscible liquids at high temperatures
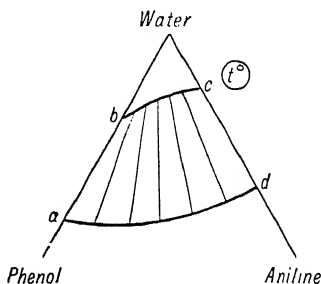
FIG. 146.   Two pairs of partially miscible liquids at low temperatures

The binodal curve will change its position according to the temperature.   In some cases, such as water, phenol and aniline system, lowering of the temperature causes the areas to spread out and form a heterogeneous band across the diagram as in Fig. 146.   Such a band is not realised in the water, alcohol, succinic nitrile system for the components freeze out before a sufficiently low temperature can be reached.

133. **Type III. Formation of Three Pairs of Partially**
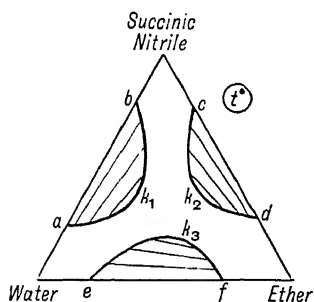
FIG. 147.   Three pairs of partially miscible liquids at high temperatures
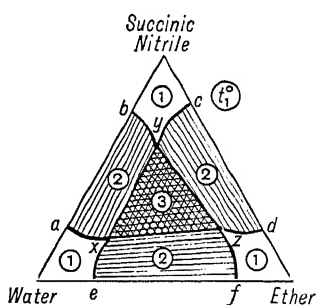
FIG. 148.   Three pairs of partially miscible liquids at low temperatures

Miscible Liquids.—Under suitable conditions water, ether and succinic nitrile can form three liquid phases, so that the

equilibrium diagram will have three binodal curves as shown in Fig. 147.

At lower temperature the binodal curves ak_1b, ck_2d and ek_3f broaden out and overlap one another as indicated in Fig. 148. A mixture having a composition represented by a point in any area marked (1) will form one homogeneous solution. Applying the Phase Rule to such a system of three components in two phases (solution and vapour) we have $F = 3$, so that the concentrations of two of the components must be fixed before the system is perfectly defined at constant temperature.

A mixture corresponding to a point in any of the areas marked (2) will separate into two liquid layers. In this case we find $F = 2$ so that it is only necessary to fix one of the concentrations in order that the system may be defined at constant temperature.

A system whose composition is represented by a point within the area (3) will break up into three liquid layers of composition, x, y and z, respectively. If we apply the Phase Rule to such a system we find $F = 1$, so that the compositions x, y and z of the three liquid layers will be fixed if the temperature is kept constant.

134. The Influence of Impurities.—The determination of the critical solution temperature of ternary mixtures has been used for testing the purity of liquids (p. 103). In the presence of an impurity such a ternary mixture will become a four-component system and the critical solution temperature will be raised or lowered according to the nature of the impurity. By determining the critical solution temperature of carbon disulphide, acetic acid and water it has been found possible to detect the presence of as little as 0·02 per cent of sulphur in the carbon disulphide. The method has also been put to use in the Crismer test for the detection of foreign fat in butter and lard.

135. Ternary Azeotropic Mixtures.—Several cases are known in which liquids form an azeotropic mixture of constant boiling point. A well-known example, discovered by Sydney Young, is the system water, ethyl alcohol and benzene.

Benzene and water are practically immiscible. Alcohol and benzene form a binary azeotropic mixture boiling at 68·2°. The three liquids together form a ternary azeotropic mixture boiling at 64·8°. The compositions and boiling points of the binary and ternary mixtures are given in the following table :

BINARY AND TERNARY AZEOTROPES
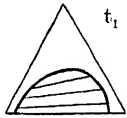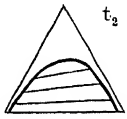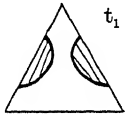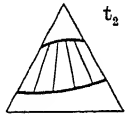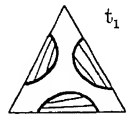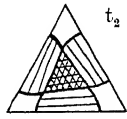
System	Ethyl Alcohol %	Water %	Benzene %	B.P.
Binary . .	95·6	4·4	. .	78·1°
Binary . .	32·4	. .	67·6	68·2
Ternary .	18·5	7·4	74·1	64·8

When any mixture of these three liquids is distilled the ternary azeotrope comes over before the boiling point of either binary azeotrope or of any of the pure components is reached.

If aqueous alcohol be mixed with benzene and the mixture subjected to distillation, the water comes over in the first fraction and anhydrous alcohol is left as residue. The azeotropic elimination of water by means of benzene may be used for preparing absolute alcohol (p. 254).

SUMMARY

Ternary Systems of Partially Miscible Liquids

System	Isothermal Diagrams	Characteristic	Example
Type I	t_1	One pair of partially miscible liquids	Chloroform, water and acetic acid
	t_2	Larger heterogeneous area at lower temperature t_2	
Type II	t_1	Two pairs of partially miscible liquids. Two binodal curves	Water, alcohol and succinic nitrile
	t_2	Heterogeneous areas spread into band at lower temperature t_2	Water, phenol and aniline
Type III	t_1	Three pairs of partially miscible liquids. Three binodal curves	Water, ether and succinic nitrile
	t_2	Heterogeneous areas overlap at lower temperature t_2. One, two or three liquid layers possible	

PRACTICAL METHODS

29. To determine the Binodal Curve for a Ternary System.—
Three components which are suitable for study at ordinary

room temperature are water, benzene and glacial acetic acid. The following experiment requires 25 c.c. of pure benzene, 125 c.c. of glacial acetic acid and a supply of distilled water. The apparatus comprises the following : 1 c.c. pipette, 5 c.c. pipette, 2 burettes, 125 c.c. conical flask and 300 c.c. conical flask.

Five c.c. of benzene is placed in the 125 c.c. flask, 1 c.c. of water is added from one burette, and the mixture treated with glacial acetic acid which is slowly added from another burette until a clear solution is obtained on vigorous shaking of the mixture. This solution is saturated with respect to the three components and the respective volumes of the components in the mixture are recorded.

Two c.c. of water is added to the liquid (which now contains 3 c.c. of water in all), and acetic acid run in with vigorous shaking until the system becomes homogeneous. Successive volumes of 3, 4, 5 and finally 6 c.c. of water are added and the mixtures treated with acetic acid until the miscibility point is attained in each case.

Two c.c. of benzene is placed in the 300 c.c. flask, and 25 c.c. of water added from the burette. Sufficient acetic acid is run in from the other burette to produce a clear solution on shaking. The same process is repeated after adding five further 25 c.c. portions of water and the volume of acetic acid required to produce homogeneity is recorded in each case.

Assuming that there is no volume change on mixing, we may calculate the volume of each component in 100 c.c. of the ternary solution at the miscibility point. These percentages are plotted on a triangular diagram and the binodal curve obtained by drawing a line through the points.

30. **Preparation of Absolute Alcohol by Azeotropic Elimination of Water.**—Although methyl alcohol may be obtained by the fractionation of the aqueous solution, the process cannot be applied to ethyl alcohol since it forms a 96 per cent azeotropic mixture with water. The last four per cent of water is usually removed in the laboratory by boiling the liquid with lime. The calcium oxide combines with the water to form calcium hydroxide and leaves pure alcohol, which is recovered by distillation.

Industrially, and for special laboratory purposes, absolute ethyl alcohol may be prepared by azeotropic elimination of the water as part of a ternary mixture consisting of 18 per

cent alcohol, 7 per cent water and 74 per cent benzene. For this purpose, benzene is added to the 96 per cent alcohol and the mixture carefully distilled. The first fraction consists of the ternary azeotrope (b.p. 65°). After all the water has been removed, the boiling point rises to about 68° and the distillate is a binary azeotrope of alcohol and benzene. After all the benzene has been removed the final distillate (b.p. 78·1°) is absolute alcohol. Absolute alcohol slowly absorbs moisture from the atmosphere and is therefore stored in sealed containers.

QUESTIONS

1. Explain the significance of the binodal curve with reference to the equilibria between chloroform, water and acetic acid.

(B.Sc., Wales.)

2. A system of three liquids A, B and C at constant temperature exhibits limited miscibility. The following table gives the compositions of co-existing liquid phases.

Phase 1			Phase 2	
%B	%C	in equilibrium with	%B	%C
88	12		13	87
82·5	12·5		12	78·5
72	14		12	64
65	15		14	52
60	16		20	48·5
50	19		39	29
46	20		43	21

Plot the isothermal diagram on the triangular graph paper provided and explain it fully. How could it be used to determine the composition of a mixture of A and B only?

Give the approximate composition of the phases into which a mixture containing 40%B and 50%C would separate.

(B.Sc. Hons., Wales.)

3. What is meant by "constant boiling mixture"? Give examples and state what use can be made of such mixtures.

(B.Sc. Hons., Manchester.)

4. Write a concise essay on fractional distillation. Explain the conditions necessary for satisfactory steam-distillation and describe Young's method for the dehydration of ethyl alcohol.

(B.Sc. Hons., Dublin.)

CHAPTER XI

SOLID AND LIQUID PHASES

Mark what unvary'd laws preserve each state,
Laws wise as Nature, and as fixed as Fate.—POPE

136. Classification of Systems.—To facilitate the discussion of the equilibria between solid and liquid phases we shall refer the systems to one of the following general classes ;

I. EUTECTIC SYSTEMS
II. TWO SALTS AND WATER

In the case of non-aqueous systems we shall consider two general types :

Type I. No Chemical Combination.
Type II. Compound Formed.

I. EUTECTIC SYSTEMS

137. Type I. No Chemical Combination.—The equilibria in a ternary system containing liquid and solid phases may be represented diagramatically by means of a right prism or space model as shown in Fig. 149 (a).

The melting points of the pure components are represented by the points A, B and C, respectively. The point e_1 is the eutectic point for the components A and B, e_2 for the components A and C, and e_3 for the components B and C.

When we add component C to the eutectic mixture of A and B at e_1, the temperature at which the solid phases A and B exist in equilibrium with the liquid phase is lowered along the curve e_1E. In the same way the curve e_2E gives the temperatures at which the solid phases A and C are in equilibrium with ternary solutions of A, B and C, while the curve e_3E represents the equilibrium between B and C and the

ternary solutions. At E, all three solid phases can exist side by side in contact with the liquid phase, and this temperature, the lowest of the series, is called the *ternary eutectic point*.

A system represented by a point in the upper part of the space diagram is entirely liquid. Below the freezing point or liquidus surfaces the pure solids and ternary liquids exist together, while below the ternary eutectic point and the corresponding solidus surface (not shown) the whole system consists of a solid mixture of the three components.

The changes in composition of the ternary mixtures can also be represented by projecting the curves e_1E, e_2E and e_3E

(a) Space Model   (b) Projection on base
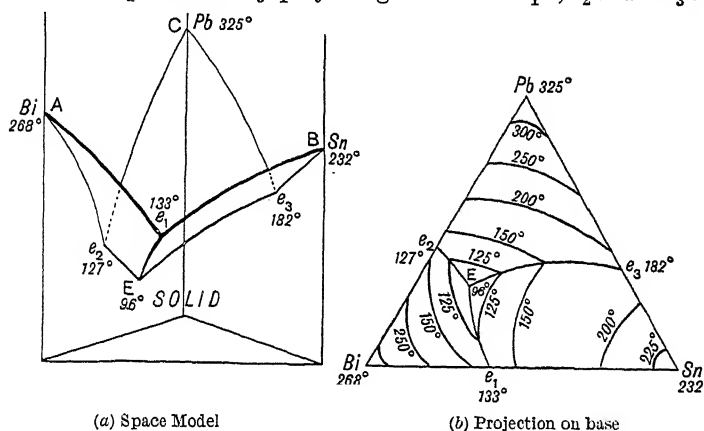
FIG. 149.   Ternary eutectic system

on to the base of the prism as shown in Fig. 149 (b). The diagram thus obtained is not an isothermal diagram, and it is necessary to specify the temperature corresponding to each point. The essential data for the system lead, bismuth and tin have been inserted in Fig. 149 (b). In virtue of its low melting point the alloy with the ternary eutectic composition is frequently used as a metal bath in the laboratory.

The cooling curve of a ternary liquid mixture shows three more or less well-defined arrests. The first arrest corresponds to the incidence of freezing and the separation of the first component ; at the second arrest the second component begins to crystallise out, and at the third arrest all three solids separate out together as a ternary eutectic mixture. If the original mixture has the exact ternary eutectic composition

the cooling curve will show one protracted arrest at the ternary eutectic temperature.   At the ternary eutectic point five phases—solid A, solid B, solid C, solution and vapour—exist in equilibrium, so that the system is invariant and freezes without change of composition at constant temperature.

138. **Type II. Compound Formed.**—If two of the components, say A and C, form a compound the space model

(a) Space Model   (b) Projection on side
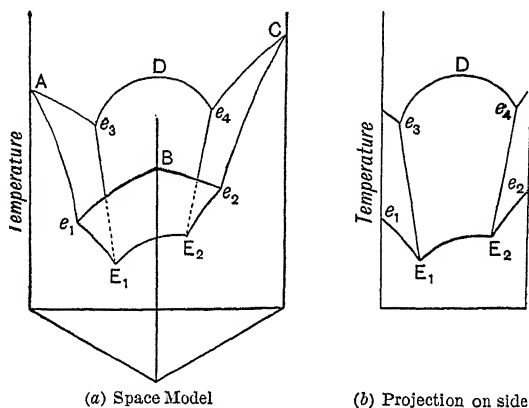
Fig. 150.   Formation of binary compound in a ternary system

assumes the form shown in Fig. 150 (a).   The maximum of the A/C binary curve gives the melting point of the pure binary compound.

In this type of system there are four binary eutectic points e_1, e_2, e_3 and e_4 and two ternary eutectic points E_1 and E_2. The eutectic mixtures separating at these points are as follows :

Point.	Eutectic Mixture.
e_1	Component A / component B
e_2	Component B / component C
e_3	Component A / compound D
e_4	Component C / compound D
E_1	Component A / component B / compound D
E_2	Component B / component C / compound D

If we apply the Phase Rule we find that these are invariant points at which the system freezes or melts without change of temperature or composition.

The curves may be projected on to the base of the prism to yield a composition diagram as described in the previous

section. Alternatively, projections may be made upon the face AC of the prism as in Fig. 150 (*b*). This is a temperature diagram which shows the effect of temperature on the various equilibria.

II. TWO SALTS AND WATER

Who would have believed thirty years ago that the Phase Rule would be today an important accessory to the manufacture of a number of heavy chemicals ? Yet the men who learnt the principles of this seemingly mathematical abstraction as students have revolutionised a great branch of chemical industry.—S. I. LEVY

139. General Classification.—A system consisting of water and two salts with a common ion is a three-component system, since the composition of every solid phase and every liquid phase can be expressed in terms of the components—salt S_1, salt S_2 and water W. Various kinds of equilibria are possible in ternary systems of this kind, but we shall confine our attention to four main classes and their more important type variations :

CLASS I. NO CHEMICAL COMBINATION.
CLASS II. DOUBLE SALT FORMED.

Type I. Double Salt not decomposed by Water.
Type II. Double Salt decomposed by Water.

CLASS III. ONE SALT FORMS A HYDRATE.

Type I. Hydrate not dehydrated by Second Salt.
Type II. Hydrate dehydrated by Second Salt.

CLASS IV. DOUBLE SALT FORMS A HYDRATE.

Type I. Hydrated Double Salt not dehydrated by Second Salt.
Type II. Hydrated Double Salt dehydrated by Second Salt.

The equilibria at any one particular temperature may be represented by means of an isothermal triangular diagram in which the side of the triangle represents 100 per cent and the corners the pure components W, S_1 and S_2.

Class I. No Chemical Combination

140. Isothermal Equilibria.—The equilibria at one particular temperature may be represented as shown in Fig. 151, where the points W, S_1 and S_2 correspond to the pure components water, salt S_1 and salt S_2, respectively. The point
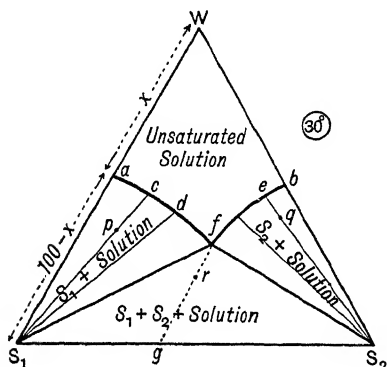
FIG. 151.   Two simple Salts and Water

a represents the solubility of S_1 in water, i.e. x grams of S_1 dissolved in $(100 - x)$ grams of water at the temperature $t°$. Similarly, the point b gives the solubility of S_2 in water at the same temperature.

Let us now examine the behaviour of a saturated solution of S_1 on the addition of increasing amounts of S_2. This we can do in the following way. Starting with an unsaturated solution of S_2 let us add S_1 so that the solution is saturated and some solid S_1 remains at the bottom of the vessel. This new solution containing all three components will be represented by the point c inside the triangle. It follows from the properties of an equilateral triangle that the distance of c from the side WS_1 gives the amount of S_2 in the solution, while its distance from the side WS_2 gives the amount of S_1 in solution.

In the next experiment a solution containing a little more S_2 is taken and again saturated with S_1. The new ternary solution will be represented by the point d, and if we proceed in this way we obtain a series of points which can be joined by the continuous curve $acdf$. All the ternary solutions corresponding to points on this curve will represent saturated solutions in equilibrium with solid salt S_1 at the temperature $t°$. To distinguish this from the ordinary tc-solubility curve it is called the *isothermal saturation curve* or more briefly, the saturation curve.

A similar saturation curve is obtained by starting with an

unsaturated solution of S_1 and adding S_2 until saturation is reached. These ternary solutions will be represented by points on the curve *bef*. At f the solution is saturated with both salts and will therefore be in equilibrium with the two solid phases S_1 and S_2. If we apply the Phase Rule to the system at this point we find $F = 1$, but since we have fixed the temperature the point is invariant.

A ternary system represented by p on the tie-line S_1c consists of an amount pc of solid S_1 and an amount S_1p of saturated solution of composition c. The tie-lines sweep out the area S_1af and any point within this region represents a univariant system of solid S_1 and a saturated solution whose composition is given by a point on the saturation curve af. The curve bf and the corresponding tie-lines have a similar significance with respect to the salt S_2, so that any point in the region S_2bf corresponds to a univariant system of solid S_2 in equilibrium with some saturated solution of composition represented by a point on the saturation curve bf. Thus, a system represented by q consists of an amount qe of solid S_2 and an amount S_2q of saturated solution of composition e.

We have seen that the system at f is saturated with respect to both S_1 and S_2. Accordingly, a point in the area S_1fS_2 represents a system of two salts in equilibrium with saturated solution of the fixed composition f. Thus the point r represents a system composed of S_2g parts of the salt S_1 and S_1g parts of the salt S_2 in equilibrium with the saturated solution of composition f.

This behaviour is exhibited by H_2O, $(NH_4)_2SO_4$ and NH_4Cl at $30°$.

141. Evaporation of Solutions.—The behaviour of a solution of the two salts during the removal of water at constant temperature (isothermal evaporation) is illustrated in Fig. 152.

If we start with an unsaturated solution at the point k and allow it to evaporate at constant temperature it will become more concentrated as the system traverses the straight line Wl, but the actual ratio of the two salts will remain unchanged. When the concentration reaches the point l the solution is just saturated with the salt S_1 which then begins to be deposited from the solution. As more water is vaporised the system will move to the point m, and at this stage the system is made up of solid S_1 and a ternary saturated solution represented by m' at the end of the tie-line through m. As more water is removed,

more and more S_1 crystallises out and the concentration of the solution moves towards the point f. When the system reaches n the solution has the concentration f and now the second salt S_2 also begins to separate. From this stage onwards S_1 and S_2 are deposited together while the solution preserves the constant composition f throughout the subsequent evaporation process. For this reason the point f is termed a " drying-up point." As the evaporation proceeds further, the system continues to traverse the straight line Wo, until at o all the water has been removed from the system and there is left a completely dry mixture consisting of S_2o parts of S_1 and S_1o parts of S_2.

Fig. 152. Evaporation of solutions of two simple salts

The evaporation of a solution represented by p will proceed in a similar manner. The salt S_2 begins to crystallise out at the point q and the concentration of the solution advances along the saturation curve towards f.

When the system reaches the point r the solution will have the composition f so that the salt S_1 also separates out. Finally, after complete removal of water the dry mixture will consist of S_2s parts of S_1 and S_1s parts of S_2.

If, however, the original unsaturated solution is represented by a point x on the straight line Wf the solution will remain unsaturated until the point f is reached when both solids begin to be deposited together. The composition of the salt mixture separating under these conditions will be given by the point y, which is the same as that of the mixture at f. The case is thus analogous with the evaporation of a solution of a single salt, for both these types of solution have only one degree of freedom.

The phenomena observed during evaporation will obviously be reversed on the gradual addition of water to a dry mixture of the salts provided the temperature is kept constant as before.

Class II. Double Salt Formed

142. **Type I. Double Salt not decomposed by Water.**—
When the components S_1 and S_2 combine to form a double
salt the isothermal diagram (Fig. 153) will comprise three
saturation curves in conformity with the principle "New
Phase–New Curve." The double salt will be represented by
the point D on the side S_1S_2 of the triangle and its composi-
tion will be S_2D parts of $S_1 : S_1D$ parts of S_2.

Starting with a binary solution of S_1 corresponding to
the point a the addition of S_2 (in the presence of excess S_1)
will lead to a series of
ternary solutions whose
compositions are given
by points on the satura-
tion curve ac. When
the point c is reached,
the salt S_2 no longer
dissolves as such but
now combines with a
definite amount of S_1 to
produce the double salt
D. The point c is in-
variant since it corres-
ponds to the existence
of two solid phases (the
simple salt S_1 and the

FIG. 153.   Double Salt not decomposed
by Water

double salt D) in equilibrium with the solution. As we add
more S_2 it continues to combine with the solid S_1 to form more
of D while the composition of the solution follows the curve
cd, the saturation curve of the double salt.

Similar behaviour is observed if we start with a binary
solution of S_2 at the point b. The composition of the ternary
solutions obtained by adding successive quantities of S_1 will
follow the curve bd, but at d the added salt will combine with
S_2 to form the compound D. The birth of a new solid phase
at d renders the system invariant at constant temperature.
At this point the solution is saturated with respect to S_2 and
D, and the addition of more S_1 will simply lead to the forma-
tion of more double salt while the concentration of the solution
traverses the curve dc.

The diagram consists of three separate saturation curves, viz. ac for solutions saturated with S_1, cd for solutions saturated with the double salt D and db for solutions saturated with S_2. The point c represents a solution saturated with the two solids S_1 and D, and the point d a solution saturated with S_2 and D. The areas have the usual significance as indicated in the diagram.

The system H_2O,$AgNO_3$ and NH_4NO_3 at $30°$ is an example of this type and the double salt which is formed has the formula $NH_4NO_3 . AgNO_3$.

If the salts S_1 and S_2 give rise to more than one double salt, each double salt will have its own characteristic saturation curve. It should be noted, however, that a double salt must exist as a true chemical compound in the solid state if it is to be registered on the phase diagram by means of a separate stability region. The fate of the salt in solution is not the concern of the Phase Rule. It is quite immaterial whether the salt dissociates into ions or associates to form complexes, but it must be capable of existing as a solid phase before it can signalise its presence by means of a separate saturation track.

Evaporation of Solutions.—The behaviour of solutions on evaporation may be predicted from the isothermal diagram (Fig. 153). Starting with an unsaturated solution represented by the point k, removal of water at constant temperature will cause the system to advance along the straight line Wm. At the point l the solid S_1 begins to crystallise out and as the separation continues, the concentration of the solution changes along the saturation curve ac. When the concentration attains that of the point c, the double salt D also begins to separate out while the solution preserves the constant composition of c.

. If the original solution has the composition n on the straight line Wo it remains unsaturated until evaporation brings the solution to the composition c when S_1 and D crystallise out simultaneously. The evaporation of a solution of this particular composition will therefore simulate that of a single salt solution.

Finally, if the original solution has the composition p on the straight line WD the double salt D is deposited at q, and the separate salts S_1 and S_2 do not appear at any stage of the process. The behaviour of such a solution is entirely analogous

with the evaporation of a solution of a simple salt. We see therefore that this system has three drying-up points c, q and d, where the composition of the solution suffers no further change as the system is evaporated to dryness.

143. Type II. Double Salt decomposed by Water.

—The behaviour of the system $H_2O, AgNO_3$ and KNO_3 at 30° is represented in Fig. 154. The curve cd is the saturation curve of the double salt $AgNO_3.KNO_3$ which exists as a solid phase at the temperature of the experiment. The position of this saturation curve within the triangle is such that the straight line DW does not meet cd, but cuts the saturation curve of potassium nitrate. This implies that
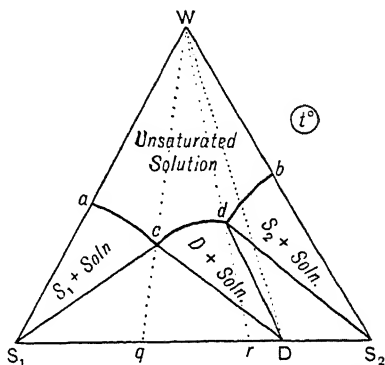
FIG. 154.   Double Salt decomposed
by Water

(a) the double salt is decomposed by water with the separation of solid KNO_3;

(b) the double salt can only exist in the stable state in contact with solutions containing excess of $AgNO_3$.

The behaviour of various solutions on evaporation may be predicted as described previously, and it is obvious that the double salt does not make its appearance unless the concentration of $AgNO_3$ and KNO_3 lies between q and r.

Class III. One Salt forms a Hydrate

144. Type I. Hydrate not dehydrated by Second Salt.

—If one of the salts, say S_1, can form a hydrate H which is stable in the presence of all amounts of S_2 there will be two saturation curves in the isothermal diagram (Fig. 155). The composition of the hydrate is represented by the point H, so that WH gives the amount of anhydrous salt and HS_1 the amount of water of crystallisation in the hydrate.

The point a represents the solubility of the hydrate H in water at the temperature $t°$. It gives, therefore, the composition of the solution in equilibrium, not with S_1, but with the solid hydrate, since this is the actual solid phase in contact with the solution. The curve bf is the saturation curve of S_2 which does not form a hydrate.

At the invariant point f, the solution is saturated with respect to both H and S_2. The areas have the significance indicated in the diagram. A point in the area HS_1S_2 represents
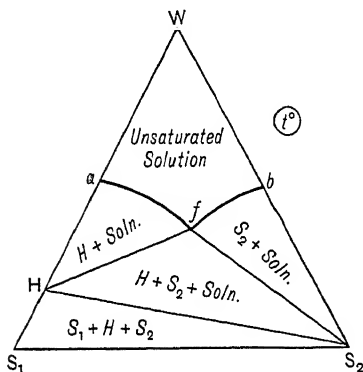
FIG. 155.   Hydrate not dehydrated by   FIG. 156.   Hydrate dehydrated by
second Salt   second Salt
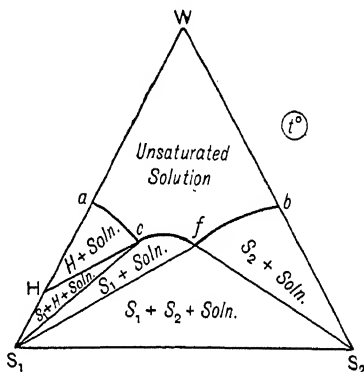
a completely solid mixture of S_1, H and S_2 for such a system does not contain sufficient water to convert all the solid S_1 into its hydrate.

The system H_2O, Na_2SO_4 and $NaCl$ at $15°$ is an example of this type and the hydrate formed is $Na_2SO_4.10H_2O$.

145. **Type II. Hydrate dehydrated by Second Salt.**—In some cases the salt S_2 may cause the dehydration of the hydrate between certain limits of concentration.

In Fig. 156 the curve ac is the saturation curve of the hydrate. With the continued addition of S_2 to a saturated solution in contact with H a point will be reached when the salt S_2 can dissolve only by the extraction of water from the hydrate. This happens at the point c, and here there will be precipitation of S_1. At this stage two solid phases, H and S_1, will be in contact with the solution. As more S_2 is added, more of the hydrate will be dehydrated and the solution will move along cf, which is the saturation curve of S_1. At the

invariant point f the solution becomes saturated with respect to S_2 also, and the curve fb is the saturation curve of S_2. The nature of the phases within the several areas is specified in the diagram.

A system which behaves in this way is H_2O, Na_2SO_4 and NaCl at 25°. At this temperature the hydrate $Na_2SO_4.10H_2O$ is dehydrated by the addition of NaCl.

The behaviour of unsaturated solutions on evaporation may be traced without difficulty in the manner indicated for the previous systems.

Class IV. Double Salt Forms a Hydrate

There is every reason to hope that a young investigator of the future will take a crystal of alum and warm it at the fire of his genius, when it will glow far into the night, revealing the chemical meaning of double salts, and most wonderful of all, the significance of water congealed by chemical forces.— T. V. BARKER

146. Type I. Hydrated Double Salt not decomposed by Water.—A simple form of isothermal diagram for such a system is shown in Fig. 157.

As before, the salt S_1 forms a hydrate H with a saturation curve ac, while the salt S_2 is anhydrous at the specified temperature $t°$. The two salts can form a hydrated double salt D of the formula $xS_1.yS_2.zW$, where x, y and z are whole numbers. These particular ratios fix the position of the point D within the triangle.

Since the hydrated

FIG. 157.   Hydrated double Salt not decomposed by Water

double salt can exist as a definite solid phase it will have its own saturation curve and its own system of tie-lines. The fact that the straight line DW cuts the saturation curve cd

shows that this hydrated double salt is not decomposed by water. The alums, such as $Na_2SO_4.Al_2(SO_4)_3.24H_2O$ behave in this way and are stable in the presence of water.

147. Type II. Hydrated Double Salt decomposed by Water.— Many systems are known in which the double salt is decomposed by water. In this case (Fig. 158) the straight line DW does not meet the saturation curve cd of the double salt.

Under certain conditions this behaviour is shown by astrakanite $MgSO_4.Na_2SO_4.4H_2O$ and it is impossible to prepare a pure solution of this double salt at 24·5°. It can exist, however, in contact with a solution containing more Na_2SO_4 than is present in the solid phase. These relationships are considered in the next section, where the effect of temperature is examined in more detail.
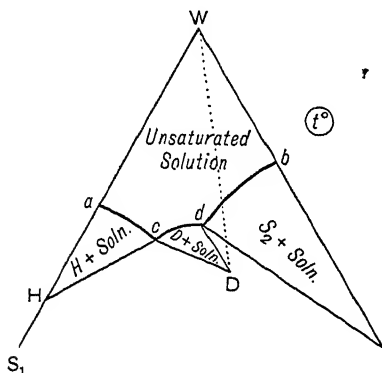
FIG. 158.   Hydrated double Salt decomposed by Water

148. Temperature and Stability of Double Salts. —The behaviour of the above systems at different temperatures may be shown by a series of separate isothermal diagrams or by means of a space model or right prism with the length representing the temperature. The essential relationships, however, may be illustrated quite simply by means of projections upon one of the sides of the prism as we have already indicated in the case ternary alloys (p. 258).

The temperature at which a double salt is formed from or breaks down into its components is the transition temperature. In the presence of water, however, double salts may behave in one of three ways :

    (*a*) the double salt is completely stable in the presence of water at all temperatures ;

    (*b*) the double salt has a lower stability limit in the presence of water ;

    (*c*) the double salt has a higher stability limit in the presence of water.

The influence of temperature in each of these cases is shown by the projection diagrams in Fig. 159. In the first type the double compound can exist in contact with the solution at all temperatures shown in the diagram. The composition of the double salt is denoted by D and the vertical dotted line from D represents solutions in equilibrium with the solid double salt. In this case, therefore, it is evident that saturated solutions formed by dissolving the double salt in water are in equilibrium with the solid double salt at all temperatures within the range of investigation. A double salt of this kind is $NH_4NO_3 \cdot AgNO_3$ which can exist in equilibrium with saturated solutions over the entire temperature range.
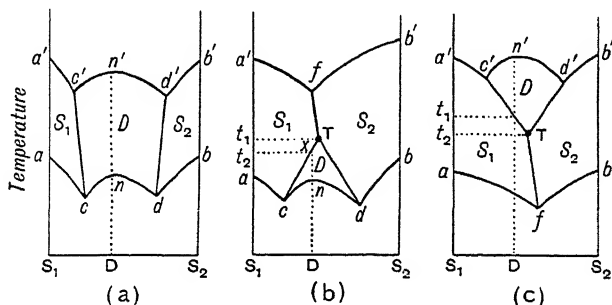
FIG. 159. Thermal stability of double Salts

In the second case (Fig. 159 (b)) the double salt has a transition point T which forms an upper limit to its existence in the system owing to the transformation

$$D \longrightarrow S_1 + S_2.$$

Above T the only solid phases which can exist are the two simple salts S_1 and S_2. The points lying between n and x on the vertical line from D represent binary systems consisting of saturated solutions in equilibrium with the double salt. Above the point x, however, this line traverses the saturation region of the simple salt S_1, but the isothermal saturation diagram corresponding to temperatures between c and T still shows three branches.

The temperature range within which the double salt is decomposed by water with the separation of one of the simple salts is defined as the *transition interval*. In the first type $(NH_4NO_3 \cdot AgNO_3)$ there is no transition interval, but in

this second case the transition interval extends from t_2 to t_1. This kind of behaviour is shown by rubidium racemate.

In the third type (Fig. 159 (c)) the transition point T forms a lower limit to the existence of the double salt. It is only above this temperature that the saturation curves show three branches corresponding to the separate existence of the individual phases S_1, D and S_2. Here the vertical dotted line from D first traverses the saturation region of the simple salt S_1 and then enters the region of double salt after passing the transition temperature T. In this case, therefore, the transition interval is represented by the range t_1 to t_2.

These diagrams enable us to understand why double salts are often unstable in the presence of water and why the evaporation of such solutions may or may not lead to the separation of the double salt according to the conditions of temperature and relative concentration.

The principles discussed in the previous sections are put to use in the manufacture of so-called heavy chemicals. In the preparation of potassium chloride from naturally-occurring carnallite $MgCl_2 . KCl . 6H_2O$, for example, it is found that if we evaporate a solution of equimolecular proportions of potassium chloride and magnesium chloride, the double salt $MgCl_2 . KCl . 6H_2O$ is not deposited until a large percentage of the potassium chloride has first separated. Indeed, to obtain carnallite as the first product of crystallisation it is essential that a large excess of magnesium chloride be present in the original solution.[1]

149. **Reciprocal Salt Pairs.**—A reciprocal salt pair is a pair of salts capable of undergoing double decomposition with the formation of another pair of salts, as indicated by the equation

$$NH_4Cl + KNO_3 \qquad KCl + NH_4NO_3.$$

Such a system contains four different salts, but is actually a three-component system since the compositions of all the phases can be expressed in terms of three of the constituents.

When such a salt pair is dissolved in water the system is then a four-component system, and the isothermal diagram may be represented by means of a square. The principles

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[1] For a more detailed treatment of these and similar systems the reader is referred to the excellent treatise by Clibbens, *The Principles of Phase Theory*, Macmillan & Co., Ltd., London. Typical investigations of ternary systems are given by Bassett *et al*, *J. Chem. Soc.*, 1933, 151.

involved in the elucidation of the equilibria in four-component systems are essentially the same as those described for the simpler ternary systems.

150. **Geological Strata.**—As Tyndal has said, " the records of geology are mainly the history of the work of water." In various parts of the world there are large areas of sedimentary deposits composed of layers of various salts and these tell the story of the physico-chemical changes which occurred in prehistoric times. The famous deposit at Stassfurt, Germany, consists of strata of carnallite $MgCl_2.KCl.6H_2O$, kieserite $MgSO_4.H_2O$, polyhalite $MgSO_4.K_2SO_4.2CaSO_4.2H_2O$, and a fourth stratum of anhydrite $CaSO_4$.
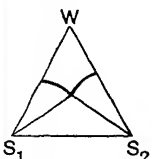
The origin of these strata was an enigma to geologists and it remained for van 't Hoff, a physical chemist, to solve the problem in the laboratory by a careful study of the equilibria between the various salts. He determined the solubilities and transition temperatures of the salts alone and in the presence of other salts by the methods described in previous chapters. In this way he was able to construct a kind of " geological thermometer " which gave to within half a degree the temperature of that prehistoric inland sea from which each stratum of salt was deposited.[1]

These masterly and painstaking researches on oceanic salt deposits created the science of experimental mineralogy and led directly to the scientific development of the German potash industry.

[1] A summary of this work is given by Stewart, *Recent Advances in Physical and Inorganic Chemistry*, 2nd edition, 1911, Longmans, Green & Co., Ltd., London.

SUMMARY

Two Salts and Water

System	Isothermal Diagram	Characteristics	Examples
Class I .		No chemical combination between the components. One " drying-up " point	H_2O, $(NH_4)_2SO_4$ and NH_4Cl

SUMMARY (*continued*)-

System	Isothermal Diagram	Characteristics	Examples
CLASS II : Type I	W S_1 D S_2	Double salt formed. Not decomposed by water. Three "drying - up" points	H_2O, NH_4NO_3 and $AgNO_3$. Double salt is $NH_4NO_3 . AgNO_3$
Type II .	W S_1 D S_2	Double salt formed. Decomposed by water. Only exists in contact with solution containing excess of one salt	H_2O, KNO_3 and $AgNO_3$. Double salt $KNO_3 . AgNO_3$ decomposed by water
CLASS III : Type I	W H S_1 S_2	One salt forms a hydrate which is not dehydrated by the second salt	H_2O, Na_2SO_4 and NaCl at 15°. The hydrate $Na_2SO_4 . 10H_2O$ not dehydrated by NaCl at 15°
Type II .	W H S_1 S_2	One salt forms a hydrate which is dehydrated by the second salt	H_2O, Na_2SO_4 and NaCl at 25°. The hydrate $Na_2SO_4 . 10H_2O$ dehydrated by NaCl at 25°
CLASS IV : Type I	W H D S_1 S_2	Hydrated double salt formed. It is not decomposed by water	Alums which are stable in the presence of water
Type II .	W H D S_1 S_2	Hydrated double salt formed. It is decomposed by water	Astrakanite $MgSO_4 . Na_2SO_4 . 4H_2O$ decomposed by water

PRACTICAL METHODS

31. **Separation of a Mixture by Fractional Crystallisation.**—
If two or more solids are soluble in the same solvent they may
be separated by the application of a process of fractional
crystallisation in which advantage is taken of the difference
in the solubility. Although the scheme adopted in a particular
case will be determined by the nature of the substances the
following outline will serve to indicate how the method may
be applied.
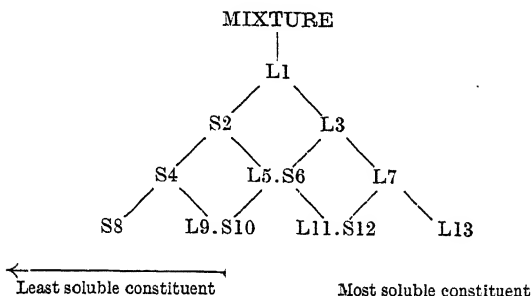
The mixture is dissolved in the solvent and the solution L1
crystallised to yield crystals designated S2 and mother-liquor
designated L3 in the above scheme. The solid S2 is dissolved
in the least amount of the hot solvent and the solution cooled
to room temperature to obtain a new crop of crystals S4 and
mother-liquor L5. The mother-liquor L5 is concentrated to
obtain crystals S6 and mother-liquor L7.

The solid S6 and mother-liquor L5 are now combined and
after heating to dissolve all the solid, the solution is crystal-
lised to obtain crystals S10 and mother-liquor L11.

The solid S4 is dissolved in the hot pure solvent and crystal-
lised to give solid S8 and mother-liquor L9, while the mother-
liquor L7 is concentrated to obtain crystals S12 and mother-
liquor L13.

The process is continued along these lines so that the least
soluble constituent moves to the left and the most soluble to
the right, while constituents of intermediate solubility lie
between these two extremes. Each crop of crystals is tested
for purity at each stage by crystallographic examination, or

by chemical or thermal analysis, and when pure takes no further part in the scheme of fractional crystallisation.[1]

QUESTIONS

1. The three substances, benzene, diphenyl and naphthalene, taken in pairs, give freezing point diagrams of the normal " eutectic curve " type. Taken all together, they form a ternary eutectic, at which liquid is simultaneously in equilibrium with all three solids. No solid solutions or compounds are formed at any temperature. The salient temperatures are as follows, all measured in degrees C.

Freezing Points	*Binary Eutectics*	*Ternary Eutectic*	
Benzene, 5°	Benzene-diphenyl, −6°	Benzene	
Diphenyl, 69°	Diphenyl-naphthalene, +39°	Diphenyl	} −20°
Naphthalene, 80°	Naphthalene-benzene, −3°	Naphthalene	

Sketch, in the form of triangular diagrams, the isothermal freezing point curves which represent the behaviour of the three-component system at 45°, 20°, −3° and −10° C. Mark each area in your sketches to indicate the number and nature of the phases which will be present in a system whose total composition is represented by a point inside the area. The vapour phase should be considered as absent and the pressure atmospheric throughout.   (B.Sc., Manchester.)

2. Explain the use of triangular diagrams to represent in three-component systems (*a*) composition (*b*) the course of crystallisation.   (Cambridge Tripos, Mineralogy.)

3. Describe the graphical methods used to represent solid-liquid equilibria for the system, $W + S_1 + S_2$ where W denotes water and S_1 and S_2 denote salts with a common ion. Sketch typical isothermal diagrams for this system (*a*) when S_1 and S_2 form neither hydrates nor double salts, (*b*) when S_1 separates only as a hydrate and S_2 only in the anhydrous condition.
                (B.Sc. Hons., Wales.)

4. Discuss the application of the Phase Rule to three-component systems with special reference to the isotherms obtained for systems of the type water-salt S_1, water-salt S_2, the two salts having an ion in common.   (B.Sc., Liverpool.)

5. Give an account of the principles involved in the investigation of the conditions of separation of double salts from solution.

[1] For details of a laboratory experiment involving the exploration of the system $KCl.HCl.H_2O$, see *J. Chem. Education*, 1937, **14**, 573.

Explain why double salts are frequently unstable in contact with water and why they do not always result from the evaporation of apparently suitable solutions. (B.Sc.Hons., Sheffield.)

6. What information about the formation of double salts can be secured by a study of the solubility of these salts and of their components in water ? (B.Sc. Hons., Bristol.)

7. If you were given what might be a double salt how would you attempt to establish whether it was a double salt or not ?

(Sub. B.Sc., Belfast.)

8. Write a short essay on Three-Component Systems.

(B.Sc., Bristol.)

9. Describe in the light of the Phase Rule the evaporation of (a) a solution of a single salt at a constant pressure, (b) a solution of two salts under isothermal conditions.

(B.Sc.Hons., Birmingham.)

10. Construct a Phase Rule diagram for the system $NH_4Cl - FeCl_3 - H_2O$ from the following analyses of saturated solutions and of the moist solids in equilibrium with them, and state what conclusions can be drawn. Analyses are expressed in grams per 100 grams of solution or mixture.

Saturated Solution		Moist Solids	
NH_4Cl	$FeCl_3$	NH_4Cl	$FeCl_3$
28·1	0	..	..
24·1	7·6	87·2	2·6
18·5	19·3	81·7	5·9
16·0	29·0	84·4	7·4
16·6	30·4	45·1	35·0
15·6	31·6	33·6	51·9
8·7	38·1	29·6	51·4
2·9	47·6	32·1	55·9
1·3	48·8	0·7	53·6
0	49·6	..	..

Atomic Weights: $N = 14$, $H = 1$, $Cl = 35·5$, $Fe = 55·8$.

(B.Sc.Hons., Wales.)

11. Give an account of the physico-chemical principles underlying (a) fractional crystallisation, (b) fractional distillation and (c) the determination of transition points. (B.Sc., Manchester.)

CHAPTER XII

LIQUID CRYSTALS

What is all science, then,
But pure religion, seeking everywhere
The true commandments, and through many forms
The eternal power that binds all worlds in one ?
—ALFRED NOYES

151. Anisotropic Liquids.—In 1888 Reinitzer found that cholesteryl benzoate showed the singular property of fusing sharply at 145° to a turbid liquid which suddenly becomes clear at 178°. On cooling the clear melt it becomes turbid at 178°, but does not become solid until the temperature is lowered to 145°. Two years later Gattermann discovered that several other substances, notably p-azoxyanisole and p-azoxyphenetole, behaved in a similar manner.

These turbid liquids are endowed with remarkable properties. They flow in the manner of ordinary liquids, but they exhibit double refraction and produce interference colours in polarised light. These optical properties imply that the molecules have a definite alignment and it was for this reason that these turbid liquids were named *liquid crystals*. Since, however, the term crystal implies an arrangement in a three-dimensional lattice these liquids are more correctly designated *anisotropic liquids*.[1] When the turbid anisotropic liquid is heated to a certain temperature it is converted into an ordinary isotropic liquid :

	116°		135°	
p-Azoxyanisole		p-Azoxyanisole		p-Azoxyanisole
(solid)		(liquid crystal)		(liquid)

Today, some hundreds of liquid crystals are known and these include many different types of compounds. All these

[1] A system is *isotropic* (from the Greek signifying *equal way*) when the properties are the same in every direction. Conversely, a system is *anisotropic* when the properties are not the same in every direction.

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compounds, however, have very long molecules, which generally contain centres of unsaturation as may be seen from the following formulae :

$$H_3C—O—\langle\rangle—N=N—\langle\rangle—O—CH_3$$

$$\uparrow$$
$$O$$

p-Azoxyanisole

$$
\begin{array}{ccccccccccccccccc}
H & H & H & H & H & H & H & H & H & H & H & H & H & H & H & H & H \\
H-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-COONa \\
H & H & H & H & H & H & H & H & H & H & H & H & H & H & H & H & H
\end{array}
$$

Sodium stearate
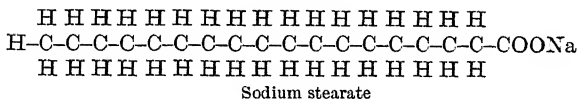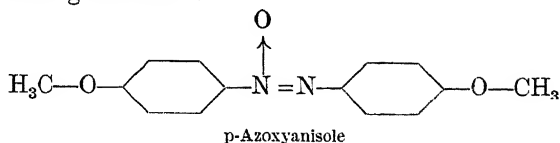
A few typical examples of liquid crystalline substances are given in the following table.

ANISOTROPIC LIQUIDS

Substance	Transition Point	Melting Point
p-Azoxyanisole	116°	135°
$CH_3OC_6H_4NONC_6H_4OCH_3$		
p-Azoxyphenetole	137°	167°
$C_2H_5OC_6H_4NONC_6H_4OC_2H_5$		
Cholesteryl Benzoate	146°	178°
$C_6H_5COOC_{27}H_{45}$		
Sodium stearate	225°	270°
$C_{17}H_{35}COONa$		
p-Methoxycinnamic Acid	170°	186°
$CH_3OC_6H_4CH : CH.COOH$		
Anisaldazine	165°	180°
$CH_3OC_6H_4CH : NN : CHC_6H_4OCH_3$		
Diethylbenzidine	115°	120°
$C_2H_5NHC_6H_4C_6H_4NHC_2H_5$		
Mercury di-(p-ethoxybenzal-aminophenyl)	204°	272°
$Hg(C_6H_4N : CHC_6H_4OC_2H_5)_2$		

152. **Change of State.**—These substances do not decompose on heating, and since the system preserves its one-component character throughout the changes, we may express the main features by means of a simple pt-diagram (Fig. 160). The diagram depicts the behaviour of p-azoxyanisole, but is mainly hypothetical inasmuch as the vapour pressures have not actually been determined. However, it will be readily understood that the curve AO_1 represents the vapour pressure of

the solid crystals, O_1O_2 the vapour pressure of the liquid crystal or anisotropic liquid and O_2B the vapour pressure

Crystalline Solid | Liquid Crystals | Ordinary Liquid

Pressure

B

O_2

O_1

Vapour

A

Temperature
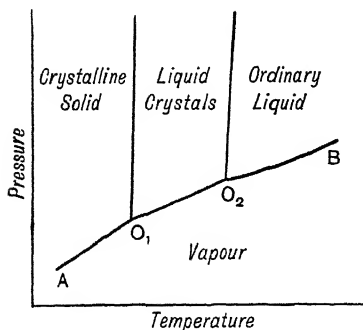
Fig. 160. pt-diagram for liquid crystals

of the isotropic liquid. There are two triple points ; at the transition point O_1 (116°) the solid crystal is converted into liquid crystal, and here the three phases solid crystal/liquid crystal/vapour are in equilibrium ; at the second triple point O_2 (135°) the three phases, liquid crystal, liquid and vapour exist together and this is called the melting point.

Although the change of state of most substances can be expressed by the familiar scheme

solid   liquid   vapour,

this is inadequate to describe the behaviour of compounds which give rise to anisotropic melts. In these cases we must take into account a fourth state of matter, viz. the liquid crystal state as indicated in the simple scheme

solid   liquid crystal   liquid   vapour.

153. **Nature of Liquid Crystals. The Swarm Theory.**—At one time it was thought that the turbid liquids obtained on fusion were heterogeneous and of the nature of emulsions, but Otto Lehmann, one of the chief pioneers in this field, was able to prove that these systems are really homogeneous and that the turbidity of the liquid in bulk is due to a simple optical effect.

The optical and magnetic properties of liquid crystals show that certain groups of molecules are oriented in certain directions. The phenomenon may be readily understood on the premises of Bose's *Swarm Theory*. When two or more molecules approach so closely that their centres are separated by a distance less than half the length of the molecule, it is obvious that free rotation will be restricted and that the molecules will tend to orient themselves in parallel formations. This idea is illustrated in Fig. 161. The random disposition

of the molecules in (a) corresponds to the isotropic liquid, and the parallel formations in (b) to the anisotropic liquid. According to Bose, swarms of molecules oriented in this fashion will be endowed with a certain symmetry and will thus simulate the behaviour of a uniaxial crystal.

Each particular swarm will appear under the microscope as a transparent liquid crystal, as Lehmann actually found. The turbid appearance of the liquid in bulk is simply due to the scattering of the light at the boundaries between the various swarms. In fact, a liquid crystal is turbid for the same reason that the transparent crystals of calcite appear opaque in a mass of marble.

The application of heat will increase the molecular motion and a continuous interchange will occur between the swarms.
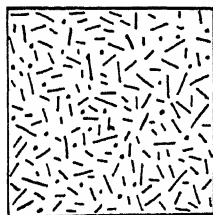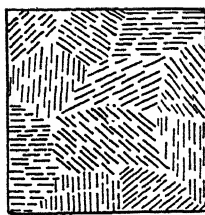
(a) Isotropic Liquid   (b) Anisotropic Liquid with Swarms

FIG. 161. Bose's swarm theory

As the temperature rises, the average size of the swarms will diminish and the temperature at which the swarms become smaller than the wave-length of light will be the " clearing point " (melting point). Above this temperature the liquid will be isotropic and singly-refracting.

The swarms are quite different from small crystals since the separate molecules can move freely about certain positions of equilibrium. One of the most striking features is the suddenness with which the liquid clears, for the above theory would seem to indicate that the clearing should be gradual, in keeping with the diminishing size of the swarms. However, it can be shown on thermodynamical grounds that if the swarms diminish in size very rapidly with rise of temperature, there will be a correspondingly rapid rise in the vapour pressure curve of the turbid liquid. This curve will therefore cut the vapour pressure curve of the isotropic liquid at a

point and the transition from anisotropic to isotropic liquid will be correspondingly sharp.

The Swarm Theory is supported by the behaviour of liquid crystals in a magnetic field. Lehmann found that a magnetic field clears the droplets of p-azoxyanisole when viewed along the lines of force as indicated in Fig. 162. When the magnetic field is cut off the liquid again becomes turbid.

Ordinary appearance   Appearance in Magnetic Field
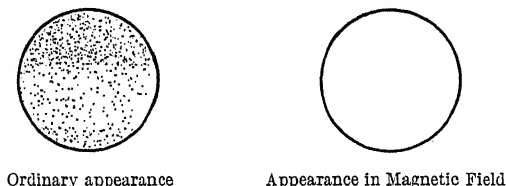
FIG. 162.   Effect of magnetic field

This behaviour may arise from the existence of a permanent magnetic moment, but it is probably more correct to say that it is due to anisotropic polarisation.

154. **Mesomorphic States.**—Chiefly as a result of the work of Lehmann, Friedel and Vorländer it is now known that there are two principal types of liquid crystal. These mesomorphic or intermediate states are called the *nematic* (or fibrous) and *smectic* (or soapy) phases, respectively. The nematic phase exhibits optical anisotropy, but otherwise behaves like a liquid of high mobility with the usual convection currents and Brownian motion. It is characterised by the appearance of mobile threads due to lines of optical discontinuity in the body of the liquid.

The smectic type is much more oily in consistency and has

FIG. 163.   Grandjean planes

limited internal mobility. This phase possesses a very complicated internal structure, and when allowed to spread over a flat surface tends to form a series of strata or terraces as depicted in Fig. 163. These terraces, called *Grandjean planes* after their discoverer, can be seen very plainly when thallium stearate is heated to the first transition point. Each layer is seen to glide between its upper and lower neighbours. The behaviour of these smectic liquids in motion is essentially different from that of true liquids. The distribution of velocity does not conform to the simple Newtonian law and since

elastic forces also come into play it is rather misleading to speak of viscosity in this connexion.

A more precise picture of these mesomorphic states may be obtained by considering the changes which occur in passing from the ordinary isotropic liquid through the intermediate stages to that of the true solid crystal. In Fig. 164 the isotropic liquid in which the molecules are moving completely at random is represented in I. In II we have the nematic state in which all the molecular axes have become parallel, but apart from this, the arrangement is irregular and the molecules can move as freely as in I. In III, which represents the smectic state, the molecules have lost one degree of freedom and are confined to a series of regularly spaced parallel surfaces. In V we have the true crystal with the molecules parallel and arranged in a three-dimensional lattice. Actually, there are two possible types : (a) the *smectogenic crystal* with the molecules arranged in planes ; this generally produces the smectic phase; (b) the *nematogenic crystal* in which the molecules interleave one another ; this gives rise to the nematic phase.

The nematic and the smectic are not the only types of liquid crystal states and one other type in particular has been known for many years. This is the *cholesteric type* which is always produced when an optically active substance forms liquid crystals. It is characterised by the production of spectral colours through reflexion of right- (or left-) handed circularly polarised light. Friedel is of the opinion that this state is a variant of the nematic type, but it also exhibits many of the properties of the smectic phase.

Friedel maintained that there were no liquid crystal phases apart from the nematic, smectic and cholesteric types, but Vorländer has stated that there are at least four intermediate states between the ordinary solid and the ordinary liquid. Indeed, Hermann has deduced on theoretical grounds that eighteen intermediate forms are possible between crystal and liquid. These states have not been observed in actual practice, but it seems to be established that states other than the normal smectic do exist. These particular states are characterised by faceted drops whose optical properties indicate a regular arrangement of molecules in each layer of the smectic substance as may be seen in IV, Fig. 164.[1]

[1] For a symposium on liquid crystals see *Trans. Faraday Soc.*, 1933, **29**, 881-1060 ; *Nature*, 1933, **132**, 86 ; *Physikal. Z.* 1937, **38**, 627.

I. **Isotropic Liquid.**
No orientation
or periodicity
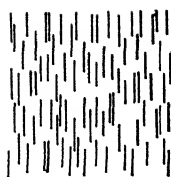
II. **Nematic Phase.**
Molecules oriented
without periodicity.
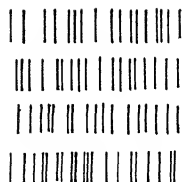
III. **Smectic Phase.**
Molecules oriented in
equispaced planes with
no internal periodicity.
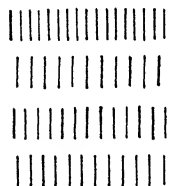
IV. **Low Temperature**
Smectic Phase.
Each layer has two-dimensional
periodicity-different for each layer.
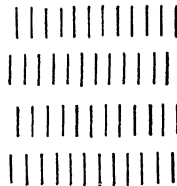
V. **Crystalline Phase.**
(a) *Smectogenic Crystal*   (b) *Nematogenic Crystal*
Complete orientation in a three-dimensional lattice.
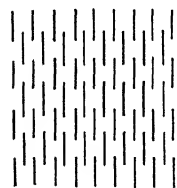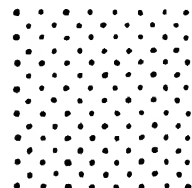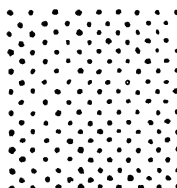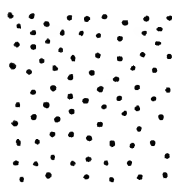
FIG. 164.   Mesomorphic states as viewed in two perpendicular
directions

155. **X-Ray Analysis of Liquid Crystals.**—The above theories have been completely confirmed by the X-ray examination of liquid crystals. The ordinary liquid gives rise to the usual " liquid haloes." The nematic phase also shows the halo effect ; although the long molecules point in one direction, they are not constrained in parallel planes and therefore do not produce a crystal pattern. The smectic phase, however, yields sharp Bragg reflexions but only in one dimension, since the molecules are disposed in parallel planes in one direction only. Finally, the true crystalline phase produces the well-known crystal pattern, for now the molecules are marshalled in a regular three-dimensional lattice.

156. **The States of Matter.**—Before the discovery of liquid crystals the change of state of a substance could be completely expressed by the scheme

SOLID CRYSTAL $\rightleftharpoons$ LIQUID $\rightleftharpoons$ VAPOUR
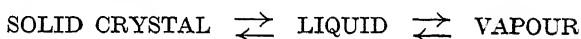
but this representation must now be extended to include the mesomorphic states :

MESOMORPHIC STATES

Nematic
CRYSTAL · · Smectic   · AMORPHOUS· · VAPOUR
Cholesteric ·
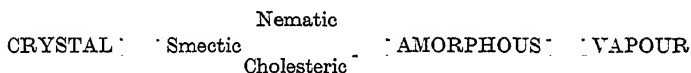
It is very probable that these curious transition phenomena occur in all substances, but it is only in the case of these long organic molecules that the temperature range of each state is sufficiently extended for actual observation with the thermal equipment available at the present time. In this connexion it should be borne in mind that the properties of these mesomorphic states are just as definite as those which characterise the crystalline and liquid, so that each of them must be regarded as a definite state of matter.

Apart from their theoretical interest liquid crystals probably play a very important rôle in Nature. It is now recognised that many commercial lubricants are more or less in the liquid crystal condition and that their efficiency largely depends upon their approach to this state. Most of the protein and fatty substance of animal bodies exists in the liquid crystal state. Indeed, this state seems to be especially suited to biological functions and may possibly be the basis of vital activity.

PRACTICAL METHODS

32. **Determination of Transition and Melting Points of Liquid Crystals.**—The experiment may be conducted in the manner of an ordinary melting point determination. Powdered *p*-azoxyanisole (or any other liquid crystalline substance) is introduced into a rather wide " melting point " tube, which is then attached to a thermometer and heated in a beaker of sulphuric acid. It will be found that the solid fuses at 116° to produce a yellowish turbid liquid which suddenly clears when the temperature is raised to 135°. The phenomena are reversed on cooling.

33. **Interference Colours in Liquid Crystals.**—According to Tutton the following materials are suitable for demonstrating the remarkable optical properties of anisotropic liquids : *p*-azoxyanisole with resin shows the phenomenon of rotating drops ; *p*-azoxyphenetole with resin gives beautiful interference colours ; cholesteryl acetate shows spherical liquid crystals. For this purpose the substance is placed on a heated slide and examined by means of a Polarising Microscope. The instrument is provided with two Nicol prisms, one serving as " polariser " and the other as " analyser," and its use depends on the fact that an isotropic material is singly refracting while an anisotropic substance is doubly refracting.[1]

Cholesteryl acetate is heated on the slide until it just melts (114°) and forms a clear liquid. It is allowed to cool slowly with the Nicols crossed, and during this process the field is quite dark because the liquid melt above 114° is an ordinary singly refracting liquid. Below 114° the liquid becomes doubly refracting and colour is observable in the microscope. With further cooling of the substance, spots of light are seen expanding to produce coloured discs with a central black cross. These discs grow in size until finally, at the transition temperature, solid crystals begin to grow and rapidly fill the field of view.

This experiment is suitable for lantern demonstration.

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[1] This instrument is also found to be very useful in phase investigations involving the rapid identification of the crystalline materials present in a system. Such applications to Phase Rule work are discussed by Hartshorn and Stewart, *Crystals and the Polarising Microscope,* Arnold & Co., 1934.

QUESTIONS

1. Discuss in detail the modern theory of liquid crystals.
(B.Sc.Hons., Edinburgh.)

2. Give an account of the properties of liquid crystals.
(B.Sc.Hons., Wales.)

3. Give an account of what is known of molecular orientation and estimate its significance in biochemistry.
(Cambridge Tripos.)

APPENDIX

A MODIFIED PHASE RULE EQUATION

> The most serious difficulty of the Phase Rule for beginners
> lies in the definition of the word " component ", of which
> many varying definitions have been given by various
> authorities.—T. W. RICHARDS

166. The Difficulties of the Phase Rule.—We have seen
that the Gibbs Phase Rule as applied to systems in equili-
brium subject to changes of temperature, pressure and con-
centration may be written in the form

where P is the number of phases, F the number of degrees of
freedom and C the number of components. In applying the
equation we have to bear in mind

- (a) that the number of components is the *minimum*
   number of constituents required to express the
   composition of each phase in the form of a chemical
   equation ;
- (b) that the restrictions imposed often cause the number
   of components to be different from the number of
   actual chemical substances in the system.

The term " component " irrevocably involves restrictions.
It has indeed to bear the brunt of the matter and assume a
responsibility not shouldered by the equation itself. It is
sometimes necessary to write out a properly balanced chemical
equation in order to decide upon the number of components,
and even then, allowance must be made for certain restric-
tions when the phases approach identity, as in critical phen-
omena, or when one of the substances is kept in a definite
weight-ratio to some other substance in the system, as in
dissociation phenomena.

167. The Modified Equation.—In view of these difficulties we may state the Phase Rule in such a way that the restrictions involved in the " component " are separately embodied in the equation itself.[1]

If we retain the original definitions of phases and degrees of freedom, and let C be the *total* number of chemical constituents (that is, actual chemical substances) present in the system, we may write

$$P + F + R = C + 2 - r,$$

where R is the number of reversible chemical reactions occurring in the system, and r, the restriction term, is equal to the number of pairs of phases having the same concentration or to the number of fixed ratios between the weights of the substances. This equation may then be applied without recourse to any process of counting or choosing components, since every chemical individual is taken into consideration. The utility of the equation will be apparent in its application to the following examples.

i. *Critical Phenomena.*—At the critical point of water, for instance, the liquid and vapour phases (one pair of phases) approach identity, so that $r = 1$. Since no chemical reaction occurs in the system, $R = 0$, and

$$2 + F + 0 = 1 + 2 - 1,$$
$$F = 0.$$

ii. *Thermal Dissociation.*—To facilitate the discussion of dissociation phenomena we may consider the following types.

Type 1. In the thermal dissociation of calcium carbonate as expressed in the equation

$$CaCO_3 \;\rightleftharpoons\; CaO + CO_2$$
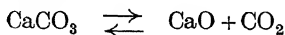
we have three chemical constituents and one reversible chemical reaction, so that

$$3 + F + 1 = 3 + 2 - 0,$$
$$F = 1.$$

Type 2.   In the system

$$NH_4Cl \;\rightleftharpoons\; NH_3 + HCl$$
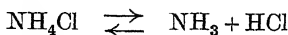
we have in addition one pair of phases (the solid phase and the

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[1] Bowden, *Nature,* 1938, **141,** 331.   For a previous attempt in the same direction see T. W. Richards, *J. Amer. Chem. Soc.,* 1916, **38,** 983.

gas phase) with identical composition. Applying the equation we find

$$2 + F + 1 = 3 + 2 - 1,$$
$$F = 1.$$

Type 3. The variance of a homogeneous system consisting of one phase may be determined in a similar manner. Thus, in the familiar case of the dissociation of steam at high temperatures

$$2 \, H_2O \quad \underset{\longleftarrow}{\overset{\longrightarrow}{}} \quad 2 \, H_2 + O_2,$$
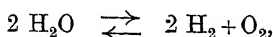
a restriction is imposed on the ratio of the concentrations of the hydrogen and the oxygen in the single phase. Accordingly,

$$1 + F + 1 = 3 + 2 - 1,$$
$$F = 2.$$

This system therefore differs from the previous types in being bivariant.

iii. *Azeotropic Mixtures.*—In the case of a binary azeotrope the compositions of the liquid and vapour are the same. Since, therefore, there is identity in one pair of phases, $r = 1$ and

$$2 + F + 0 = 2 + 2 - 1,$$
$$F = 1.$$

The azeotrope will thus distil at constant temperature if the pressure is kept constant.

iv. *Maximum and Minimum Melting Solid Solutions.*—Assuming that the system contains the substances A and B, we have for the solid solution of maximum or minimum melting point

$$2 + F + 0 = 2 + 2 - 1,$$
$$F = 1.$$

This particular solid solution will therefore melt at constant temperature if the pressure is kept constant.

v. *Meritectic and Peritectic Reactions.*—The equation also leads to a clear differentiation between physical and chemical change in transition processes. We know, for example, that the system

$$Na_2SO_4 . 10 \, H_2O \qquad Na_2SO_4 + \text{liquid},$$

containing three substances (decahydrate, anhydrous salt

and water), is invariant, so that $F = 0$. We may now use the equation to determine the value of R,

$$4 + 0 + R = 3 + 2 - 0,$$
$$R = 1.$$

The point is thus an incongruent melting point arising from the rupture or formation of chemical linkages. A similar kind of meritectic reaction is exhibited by an intermetallic compound with a submerged maximum, as, for example,

$$AuSn_4 \; \underset{\longleftarrow}{\overset{\longrightarrow}{}} \; AuSn_2 + liquid.$$
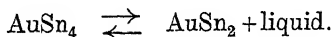
Here the three substances are $AuSn_4$, $AuSn_2$ and Sn, but in this case the linkages involved are metallic.

If we apply the equation to a binary system of two solid solutions undergoing peritectic reaction,

$$a \; \underset{\longleftarrow}{\overset{\longrightarrow}{}} \; \beta + liquid,$$
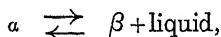
we have

$$4 + 0 + R = 2 + 2 - 0,$$
$$R = 0.$$

It is clear, therefore, that the peritectic transformation of solid solutions does not involve the rupture of chemical or metallic linkages.

The modified equation, while removing the bugbear of the term " component," is easy to apply and is also of utility in other directions.

INDEX

THE END